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(11) Publication number: **0 518 238 A1**

(12)

## EUROPEAN PATENT APPLICATION

(21) Application number: **92109588.1**

(51) Int. Cl.5: **C07D 487/04**

(22) Date of filing: **05.06.92**

(30) Priority: **07.06.91 JP 162324/91**  
**27.11.91 JP 311212/91**  
**27.11.91 JP 335861/91**  
**21.02.92 JP 69980/92**

(43) Date of publication of application:  
**16.12.92 Bulletin 92/51**

(94) Designated Contracting States:  
**CH DE FR GB LI NL**

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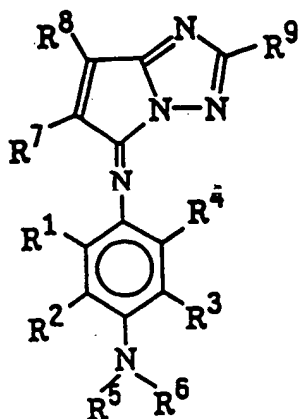
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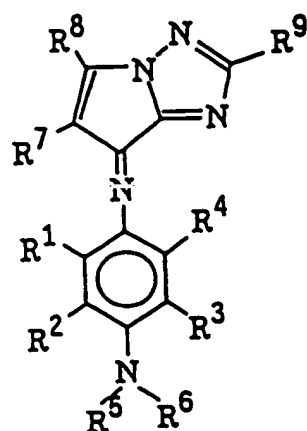
(54) **Pyrrolotriazole derivative.**

(57) A novel pyrrolotriazole derivative is disclosed, represented by any one of formulae (I), (II), or (III):

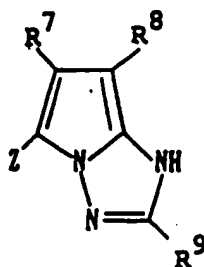
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(I)



(II)



(III)

wherein:

R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> each independently represents a hydrogen atom or a nonmetallic atomic group;

R<sup>5</sup> and R<sup>6</sup> each independently represents a hydrogen atom, alkyl group, an aryl group, or a heterocyclic group;

R<sup>7</sup> represents an electrophilic group having a Hammett's substituent constant  $\sigma_p$  of 0.15 or more;

R<sup>8</sup> and R<sup>9</sup> each independently represents a hydrogen atom or a nonmetallic atomic group;

the sum of Hammett's substituent constant  $\sigma_p$  of R<sup>7</sup> and R<sup>8</sup> is 0.65 or more;

R<sup>1</sup> and R<sup>2</sup>, and/or R<sup>2</sup> and R<sup>5</sup>, and/or R<sup>5</sup> and R<sup>6</sup>, and/or R<sup>6</sup> and R<sup>3</sup>, and/or R<sup>3</sup> and R<sup>4</sup> may be connected to each other to form a cyclic structure;

R<sup>7</sup> and R<sup>8</sup> may be connected to each other to form a cyclic structure; and

Z represents a hydrogen atom, a halogen atom, an arylthio group, a heterocyclic thio group, an arylsulfinyl group, or a nitroso group.

The present invention relates to a novel pyrrolotriazole derivative

1H-Pyrrolo-[1,2-b][1,2,4]triazole derivatives are useful as synthesis intermediates of physiologically active substances such as pharmaceutical preparations and pesticides. These derivatives are also known as coupler nuclei and dyes which exhibit reduced secondary absorption in the field of photographic chemistry (proceedings of the 60th Annual Conference of The Society of Photographic Science and Technology of Japan). However, 1H-pyrrolo-[1,2-b][1,2,4]triazole dyes which have heretofore been known exhibit a maximum absorption wavelength of lower than 560 nm. No 1H-pyrrolo-[1,2-b][1,2,4]triazole dyes which exhibit a maximum absorption wavelength of higher than 600 nm have been known.

In recent years, 1H-pyrrolo-[1,2-b][1,2,4]triazole dyes which exhibit a maximum absorption wavelength of higher than 560 nm, particularly 600 nm have been desired. In other words, dyes containing a 1H-pyrrolo-[1,2-b][1,2,4]triazole nucleus which exhibit reduced secondary absorption and a primary absorption wavelength of higher than 600 nm have been keenly desired.

Furthermore, in recent years, new color image formation methods such as color electrophotography, ink jet printing process and heat-sensitive transfer process have been proposed. On the other hand, with the development of electronic imaging technique, the demand for solid state image pick-up tube and filter for color liquid crystal television set has increased. Thus, azomethine dyes have been applied and reviewed in color photography as well as various systems or merchandise.

As cyan azomethine dyes in these applications there have been known phenol and naphthol azomethine dyes. Furthermore, imidazole azomethine dyes and hydroxypyridine azomethine dyes have been known.

Moreover, pyrazoloazole azomethine dyes, pyrazolopyrimidin-5-one azomethine dyes, pyrazoloquinazolinone azomethine dyes, pyrazolotriazine azomethine dyes and cyan azomethine dyes have been known.

However, these known azomethine dyes have various disadvantages. For example, phenol and naphthol azomethine dyes exhibit too broad an absorption to serve as dyes for filter. Further, imidazole azomethine dyes are disadvantageous in that they exhibit a low fastness to light. Moreover, pyrazolopyrimidin-5-one azomethine dyes, pyrazoloquinazolinone azomethine dyes and pyrazolotriazine azomethine dyes exhibit too broad an absorption. Further, pyrazolotriazole azomethine dyes exhibit a low fastness to light. Moreover, hydroxypyridine azomethine dyes can hardly be synthesized and exhibit a low fastness to light.

Thus, among known azomethine dyes, there are no dyes which exhibit an absorption waveform suitable for cyan color and a high fastness to light and heat. Therefore, the development of azomethine dyes which exhibit a sharp absorption and a high fastness has been keenly desired.

In order to overcome these difficulties, the inventors made a study on novel azomethine dyes. As a result, it was found that pyrrolotriazole azomethine dyes having a specific structure which has never been known exhibit a sharp absorption and a high fastness to light. Thus, the present invention was worked out.

Pyrrolotriazole couplers are disclosed in JP-A-62-279340 and 62-278552 (the term "JP-A" as used herein means an "unexamined published Japanese patent application").

Even if the foregoing techniques are known, the present invention is by no means limited thereby.

The above mentioned known couplers are considered to undergo color development to produce azomethine dyes. According to the above cited references, the color of the dyes thus produced are magenta.

The inventors' study showed that pyrrolotriazole azomethine dyes represented by formulae (I) and (II) given later exhibit a cyan color when its coupler portion is such that Hammett's substituent constant  $\sigma_p$  of  $R^7$  is 0.15 or more and the sum of Hammett's substituent constant  $\sigma_p$  of  $R^7$  and  $R^8$  is 0.65 or more.

In the above cited references, there is no reference to couplers which will give an azomethine dye that exhibits a cyan color. There is neither reference that gives an expectation of a specific structure that exhibits a cyan color.

In other words, it was disclosed for the first time by the inventors, who made a study on the relationship between the substituents  $R^7$  and  $R^8$  and the absorption characteristics of dye, that novel pyrrolotriazole azomethine dyes of the present invention exhibit an excellent cyan color. It is extremely difficult to expect this fact from the above cited references.

It is therefore an object of the present invention to provide a novel pyrrolotriazole derivative.

It is another object of the present invention to provide a pyrrolotriazole azomethine dye which exhibits a sharp absorption and a high fastness to heat and light.

These and other objects of the present invention will become more apparent from the following detailed description and examples.

These objects of the present invention are accomplished with pyrrolotriazole derivatives represented by formulae (I) to (III):

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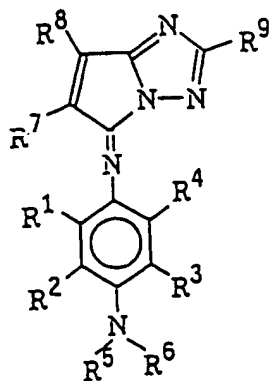
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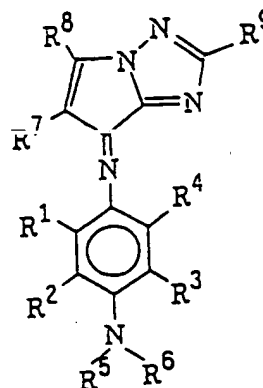
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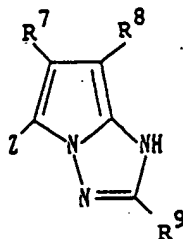
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(I)



(II)



(III)

In the above formulae (I) to (III), R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> each independently represents a hydrogen atom or nonmetallic atomic group.

R<sup>5</sup> and R<sup>6</sup> each independently represents a hydrogen atom, alkyl group, aryl group or heterocyclic group.

R<sup>7</sup> represents an electrophilic group having a Hammett's substituent constant  $\sigma_p$  of 0.15 or more.

R<sup>8</sup> and R<sup>9</sup> each independently represents a hydrogen atom or nonmetallic atomic group.

The sum of Hammett's substituent constant  $\sigma_p$  of R<sup>7</sup> and R<sup>8</sup> is 0.65 or more.

R<sup>1</sup> and R<sup>2</sup>, and/or R<sup>2</sup> and R<sup>5</sup>, and/or R<sup>5</sup> and R<sup>6</sup>, and/or R<sup>6</sup> and R<sup>3</sup>, and/or R<sup>3</sup> and R<sup>4</sup> may be connected to each other to form a cyclic structure.

R<sup>7</sup> and R<sup>8</sup> may be connected to each other to form a cyclic structure.

Z represents a hydrogen atom, halogen atom, arylthio group, heterocyclic thio group, arylsulfinyl group or nitroso group.

Fig. 1 shows the absorption spectrum of ethyl acetate solution of exemplary Compound (I-2) and a comparative dye a.

Among the compounds represented by formulae (I) to (III), those represented by formulae (I) and (II) are useful as cyan dyes.

Further, the 1H-pyrrolo-[1,2-b][1,2,4]triazole derivatives represented by formula (III) are useful as synthesis intermediates of the compounds represented by formulae (I) and (II), or physiologically active substances such as pharmaceutical preparations and pesticides.

Formulae (I) to (III) will be further described hereinafter.

Hammett's substituent constant as used herein will be now briefly discussed. Hammett's rule is an empirical law which was proposed in 1935 by L. P. Hammett to give a quantitative discussion of the effect of substituents on the reaction or equilibrium of benzene derivatives. This rule is now widely considered reasonable. Substituent constants determined by Hammett's rule include  $\sigma_p$  value and  $\sigma_m$  value which can be found in many general references, e.g., J.A. Dean, *Lange's Handbook of Chemistry*, vol. 12, 1979 (McGraw-Hill), and *Kagaku No Ryoiki (The Domain of Chemistry)*, extra edition, No. 122, pp. 98 - 103, 1979 (Nankodo). In the present invention, various substituents are limited or illustrated by Hammett's substituent constant  $\sigma_p$ . However, this doesn't mean that these substituents are limited to those having known  $\sigma_p$  values found in the above cited references. It goes without saying that even when these substituents exhibit  $\sigma_p$  values unknown in any reference, they are included in those having  $\sigma_p$  values that would be included in the range known in these references when measured according to Hammett's rule. The value of  $\sigma_p$  will be hereinafter defined in this manner.

$R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  each independently represents a hydrogen atom or nonmetallic atomic group. Examples of the nonmetallic atomic group include halogen atom, alkyl group, aryl group, heterocyclic group, cyano group, hydroxyl group, nitro group, carboxyl group, sulfonic acid group, amino group (including substituted amino group), alkoxy group, aryloxy group, acylamino group, aminocarbonylamino group, sulfamoylamino group, alkylthio group, arylthio group, alkoxycarbonylamino group, sulfonycarbonylamino group, carbamoyl group, sulfamoyl group, sulfonyl group, alkoxycarbonyl group, heterocyclic oxy group, azo group, acyloxy group, carbamoyloxy group, silyloxy group, aryloxy carbonyl group, imido group, heterocyclic thio group, sulfinyl group, phosphoryl group, formyl group, acyl group, and azoyl group. Of these non-metallic atomic groups, those which can contain substituents may be substituted by substituents such as halogen atom, hydroxyl group, carboxyl group, sulfo group, cyano group, nitro group, amino group, alkyl group, alkenyl group, alkynyl group, aryl group, alkoxy group, aryloxy group, alkylthio group, arylthio group, alkylsulfonyl group, arylsulfonyl group, acyl group, acyloxy group, alkoxycarbonyl group, aryloxy carbonyl group, carbonamido group, sulfonamido group, carbamoyl group, sulfamoyl group, ureido group, alkoxycarbonylamino group, sulfamoylamino group, alkoxysulfonyl group, imido group and heterocyclic group (these substituents will be hereinafter referred to as "substituent group A").

Specific examples of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  include hydrogen atom, alkyl group (preferably alkyl group having a total carbon atom number of from 1 to 30 (hereinafter expressed as " $C_{1-30}$  alkyl group"), e.g., methyl, ethyl, propyl, butyl), alkoxy group (preferably  $C_{1-30}$  alkoxy group, e.g., methoxy, ethoxy, methoxyethoxy, isopropoxy), halogen atom (e.g., bromine, fluorine, chlorine), acylamino group (preferably  $C_{1-30}$  alkylcarbonylamino group, e.g., formylamino, acetylamino, propionylamino, cyanoacetylamino, or preferably  $C_{7-30}$  arylcarbonylamino group, e.g., benzoylamino, p-toluylamino, pentafluorobenzoylamino, m-methoxybenzoylamino), alkoxycarbonyl group (preferably  $C_{2-30}$  alkoxycarbonyl group, e.g., methoxycarbonyl, ethoxycarbonyl), cyano group, sulfonylamino group (preferably  $C_{1-30}$  sulfonylamino group, e.g., methanesulfonylamino, ethanesulfonylamino, N-methylmethanesulfonylamino), carbamoyl group (preferably  $C_{2-30}$  carbamoyl group, e.g., methylcarbamoyl, dimethylcarbamoyl, butylcarbamoyl, isopropylcarbamoyl, t-butylcarbamoyl, cyclopentylcarbamoyl, cyclohexylcarbamoyl, methoxyethylcarbamoyl, chloroethylcarbamoyl, cyanoethylcarbamoyl, ethylcyanoethylcarbamoyl, benzylcarbamoyl, ethoxycarbonylmethylcarbamoyl, furfurylcarbamoyl, tetrahydrofurfurylcarbamoyl, phenoxymethylcarbamoyl, allylcarbamoyl, crotylcarbamoyl, prenylcarbamoyl, 2,3-dimethyl-2-butenylcarbamoyl, homoallylcarbamoyl, homocrotylcarbamoyl, homoprenylcarbamoyl, preferably  $C_{7-30}$  arylcarbamoyl group, e.g., phenylcarbamoyl, p-toluylcarbamoyl, m-methoxyphenylcarbamoyl, 4,5-dichlorophenylcarbamoyl, p-cyanophenylcarbamoyl, p-acetylamino phenylcarbamoyl, p-methoxycarbonylphenylcarbamoyl, m-trifluoromethylphenylcarbamoyl, o-fluorophenylcarbamoyl, 1-naphthylcarbamoyl, or preferably  $C_{4-30}$  heterylcarbamoyl group, e.g., 2-pyridylcarbamoyl, 3-pyridylcarbamoyl, 4-pyridylcarbamoyl, 2-thiazolylcarbamoyl, 2-benzthiazolylcarbamoyl, 2-benzimidazolylcarbamoyl, 2-(4-methylphenyl)-1,3,4-thiazolylcarbamoyl), sulfamoyl group (preferably  $C_{6-30}$  sulfamoyl group, e.g., methylsulfamoyl, dimethylsulfamoyl), aminocarbonylamino group (preferably  $C_{1-30}$  aminocarbonylamino group, e.g., methylaminocarbonylamino, dimethylaminocarbonylamino), alkoxycarbonylamino group (preferably  $C_{2-30}$  alkoxycarbonylamino group, e.g., methoxycarbonylamino, ethoxycarbonylamino), hydroxyl group, carboxyl group (including salts thereof), sulfonic acid group (including salts thereof), amino group (preferably  $C_{6-30}$  amino group, e.g., amino, methylamino, dimethylamino, anilino), aryl group (preferably  $C_{6-30}$  aryl group, e.g., phenyl, m-acetylphenyl, p-methoxyphenyl), heterocyclic group (preferably  $C_{3-30}$  heterocyclic group, e.g., 2-pyridyl, 2-furyl, 2-tetrahydrofuryl), nitro group, aryloxy group (preferably  $C_{6-30}$  aryloxy group, e.g., phenoxy, p-methoxyphenoxy, o-chlorophenoxy), sulfamoylamino group (preferably  $C_{6-30}$  sulfamoylamino group, e.g., methylsulfamoyl, dimethylsulfamoyl), alkylthio group (preferably  $C_{1-30}$  alkylthio group, e.g., methylthio, ethylthio), arylthio group (preferably  $C_{6-30}$  arylthio group, e.g., phenylthio, p-methoxyphenylthio, o-chlorophenylthio), sulfonyl group (preferably  $C_{1-30}$  sulfonyl group, e.g.,

methanesulfonyl, p-toluenesulfonyl), formyl group, acyl group (preferably C<sub>1-30</sub> acyl group, e.g., acetyl, benzoyl, p-toluyyl), heterocyclic oxy group (preferably C<sub>3-30</sub> heterocyclic oxy group), azo group (preferably C<sub>3-30</sub> azo group, e.g., p-nitrophenylazo), acyloxy group (preferably C<sub>1-30</sub> acyloxy group, e.g., acetyloxy, benzoyloxy), carbamoyloxy group (preferably C<sub>1-30</sub> carbamoyloxy group, e.g., methylcarbamoyloxy),  
 5 silyloxy group (preferably C<sub>3-30</sub> silyloxy group, e.g., trimethylsilyloxy), aryloxy carbonyl group (preferably C<sub>7-30</sub> aryloxy carbonyl group, e.g., phenoxycarbonyl), imido group (preferably C<sub>4-30</sub> imido group, e.g., phthalimido), heterocyclic thio group (preferably C<sub>3-30</sub> heterocyclic thio group), sulfinyl group (preferably C<sub>1-30</sub> sulfinyl group, e.g., diethylaminosulfinyl), phosphoryl group (preferably C<sub>6-30</sub> phosphoryl group, e.g., diamminophosphoryl), and azolyl group (preferably C<sub>2-30</sub> azolyl group, e.g., 2-pyrazolyl).

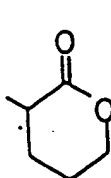
10 Preferred among the groups represented by R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> is hydrogen atom.

Preferred among the groups represented by R<sup>1</sup> are hydrogen atom, C<sub>1-30</sub> alkyl group, C<sub>1-30</sub> alkoxy group, halogen atom (e.g., fluorine, chlorine, bromine), C<sub>1-30</sub> acylamino group, C<sub>1-30</sub> sulfonylamino group, C<sub>1-30</sub> aminocarbonylamino group, and C<sub>2-30</sub> alkoxycarbonylamino group. Particularly preferred among these groups are hydrogen atom, alkyl group, and acylamino group.

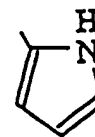
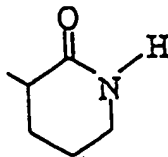
15 R<sup>5</sup> and R<sup>6</sup> each independently represents a hydrogen atom, alkyl group, aryl group, or heterocyclic group. The alkyl group, aryl group, and heterocyclic group may be substituted by substituents such as substituent group A.

Specific examples of R<sup>5</sup> and R<sup>6</sup> include a hydrogen atom, alkyl group (preferably C<sub>1-30</sub> alkyl group, e.g., methyl, ethyl, propyl, isopropyl, butyl, octyl, 2-aminoethyl, 2-carbamoylethyl, 2-carboxyethyl, 4-  
 20 sulfobutyl, 3-(4-methoxyphenoxy)propyl, 2-methanesulfonamidoethyl, 2-hydroxyethyl, 3-hydroxypropyl, 4-hydroxybutyl, 2-methoxyethyl, 3-methoxypropyl, ethoxyethyl, 2-phenylethyl, 2-cyanoethyl, cyanomethyl, 2-chloroethyl, 3-bromopropyl, 2-methoxycarbonylethyl, 3-ethoxycarbonylpropyl, 2-(N-methylaminocarbonyl)-ethyl, 3-(N,N-dimethylaminocarbonyl)propyl, 2-acetylaminoethyl, 3-(ethylcarbonylamino)propyl, allyl homoal-  
 25 lyl, prenyl, n-dodecyl, 2-acetyloxyethyl), aryl group (preferably C<sub>6-30</sub> aryl group, e.g., phenyl, p-tolyl, p-methoxyphenyl, 2,4-dichlorophenyl, p-nitrophenyl, 2,4-dicyanophenyl, 2-naphthyl) or heterocyclic group (including those containing substituents, preferably C<sub>3-30</sub> heterocyclic group such as those represented by the following formulae).

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40 Preferred among the groups represented by R<sup>5</sup> and R<sup>6</sup> is a C<sub>1-30</sub> alkyl group which may be substituted (e.g., methyl, ethyl, propyl, 2-cyanoethyl, 2-acetyloxyethyl, 2-ethoxycarbonylethyl, 2-methoxyethyl, 2-methanesulfonamidoethyl, 2-hydroxyethyl, 3-hydroxypropyl, allyl, homoallyl, prenyl).

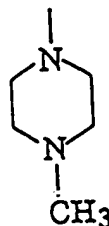
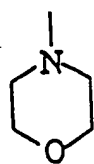
Examples of the ring which R<sup>5</sup> and R<sup>6</sup> may be connected to each other to form include those represented by the following formulae:

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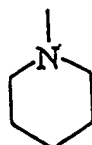
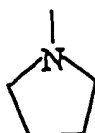
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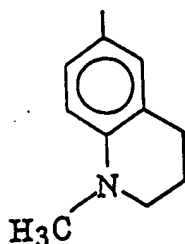
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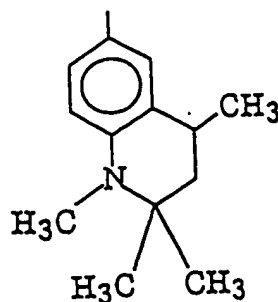
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Preferred examples of the ring which  $R^2$  and  $R^5$ , and/or  $R^3$  and  $R^6$ , may be connected to each other to form include those represented by the following formulae:

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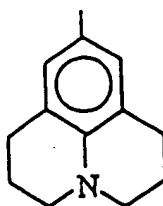


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$R^7$  represents an electrophilic group having a Hammett's substituent constant  $\sigma_p$  of 0.15 or more.

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Examples of  $R^7$  include formyl group, acyl group, acyloxy group, carbamoyl group, alkoxy carbonyl group, aryloxy carbonyl group, cyano group, carboxyl group, nitro group, dialkylphosphono group, diarylphosphono group, diarylphosphinyl group, alkylsulfinyl group, arylsulfinyl group, alkylsulfonyl group, arylsulfonyl group, arylthio group, sulfonyloxy group, acylthio group, sulfamoyl group, isocyanato group, thiocyanato group, thiocarbonyl group, alkyl group substituted by at least two halogen atoms, alkoxy group substituted by at least two halogen atoms, aryloxy group substituted by at least two halogen atoms, alkylamino group substituted by at least two halogen atoms, alkylthio group substituted by at least two halogen atoms, aryl group substituted by other electrophilic groups having a Hammett's substituent constant  $\sigma_p$  of 0.15 or more, heterocyclic group, chlorine atom, bromine atom, and selenocyanato group. Of these groups, those which can contain substituents may be substituted by substituents such as substituent group A.

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Specific examples of  $R^7$  include acyl group (e.g., acetyl, 3-phenylpropanoyl, benzoyl, 4-dodecyloxybenzoyl), acyloxy group (e.g., acetoxy), carbamoyl group (e.g., N-ethylcarbamoyl, N,N-dibutylcarbamoyl, N-(2-

dodecyloxyethyl)carbamoyl, N-methyl-N-dodecylcarbamoyl, N-[3-(2,4-di-t-amyloxy)propyl]carbamoyl, alkoxycarbonyl group (preferably straight-chain, branched or cyclic alkoxycarbonyl group, e.g., methoxycarbonyl, ethoxycarbonyl, isopropoxycarbonyl, isobutoxycarbonyl, n-octyloxycarbonyl, n-decyloxycarbonyl, n-dodecyloxycarbonyl, n-hexadecyloxycarbonyl, 2-ethylhexyloxycarbonyl, 3,5,5-trimethylhexyloxycarbonyl, 2-ethyl-4-methylpentyloxycarbonyl, 2-hexyldecyloxycarbonyl, 2-heptylundecyloxycarbonyl, 2-octyldodecyloxycarbonyl, 2,4,6-trimethylheptyloxycarbonyl, 2,4,6,8-tetramethylnonyloxycarbonyl, benzyloxycarbonyl, 2-phenethyloxycarbonyl, 3-(t-octylphenoxy)propoxycarbonyl, 3-(2,4-di-t-pentylphenoxy)propoxycarbonyl, 2-(4-isopropenyloxy)ethoxycarbonyl, 3-dodecyloxypropoxycarbonyl, 2-dodecylthioethoxycarbonyl, 9,10-epoxyoctadecyloxycarbonyl, dodecyloxycarbonylmethoxycarbonyl, 2-(2-naphthylthio)ethoxycarbonyl, 7,7-dimethyl-2-(3',3'-dimethylbutyl)-5-methyloctyloxycarbonyl, 2-methyl-cyclohexyloxycarbonyl, 2-hexyl-cyclohexyloxycarbonyl, aryloxycarbonyl group (e.g., phenoxycarbonyl), cyano group, carboxyl group, nitro group, dialkylphosphono group (e.g., dimethylphosphono), diarylphosphono group (e.g., diphenylphosphono), diarylphosphinyl group (e.g., diphenylphosphinyl), alkylsulfinyl group (e.g., 3-phenoxypropylsulfinyl), arylsulfinyl group (e.g., 3-pentadecylphenylsulfinyl), alkylsulfonyl group (e.g., methanesulfonyl, octanesulfonyl), arylsulfonyl group (e.g., benzenesulfonyl, toluenesulfonyl), alkylthio group (e.g., methylthio, octylthio, tetradecylthio, 2-phenoxyethylthio, 3-phenoxypropylthio, 3-(4-t-butylphenoxy)propylthio), arylthio group (e.g., phenylthio, 2-butoxy-5-t-octylphenylthio, 3-pentadecylphenylthio, 2-carboxyphenylthio, 4-tetradecanamidophenylthio), sulfonyloxy group (e.g., methanesulfonyloxy, toluenesulfonyloxy), acylthio group (e.g., acetylthio, benzoylthio), sulfamoyl group (e.g., N-ethylsulfamoyl, N,N-dipropylsulfamoyl, N-(2-dodecyloxyethyl)-sulfamoyl, N-ethyl-N-dodecylsulfamoyl, N,N-diethylsulfamoyl), isocyanato group, thiocyanato group, thiocarbonyl group (e.g., methylthiocarbonyl, phenylthiocarbonyl), alkyl group substituted by at least two halogen atoms (e.g., trifluoromethane, heptafluoropropane), alkoxy group substituted by at least two halogen atoms (e.g., trifluoromethoxy), aryloxy group substituted by at least two halogen atoms (e.g., pentafluorophenyl), alkylamino group substituted by at least two halogen atoms (e.g., N,N-di(trifluoromethyl)amino), alkylthio group substituted by at least two halogen atoms (e.g., difluoromethylthio, 1,1,2,2-tetrafluoroethylthio), aryl group substituted by two or more electrophilic groups having a Hammett's substituent constant  $\sigma_p$  of 0.15 or more (e.g., 2,4-dinitrophenyl, 2,4,6-trichlorophenyl, pentachlorophenyl), heterocyclic group (e.g., 2-benzoxazolyl, 2-benzothiazolyl, 1-phenyl-2-benzimidazolyl, 5-chloro-1-tetrazolyl, 1-pyrrolyl), chlorine atom, bromine atom, and selenocyanato group.

Among these substituents, those which can further contain substituents may further contain halogen atoms or substituents connected via carbon atom, oxygen atom, nitrogen atom or sulfur atom thereto.

Examples of  $\sigma$  values of typical electrophilic groups having a Hammett's substituent constant  $\sigma_p$  of 0.15 or more include 0.66 for cyano group, 0.45 for carboxyl group, 0.78 for nitro group, 0.54 for trifluoromethyl group, 0.50 for acetyl group, 0.92 for trifluoromethanesulfonyl group, 0.72 for methanesulfonyl group, 0.70 for benzenesulfonyl group, 0.49 for methanesulfinyl group, 0.36 for carbamoyl group, 0.45 for methoxycarbonyl group, 0.44 for phenoxycarbonyl group, 0.37 for pyrazolyl group, 0.36 for methanesulfonyloxy group, 0.33 for benzenesulfonyloxy group, 0.60 for dimethoxyphosphoryl group, 0.57 for sulfamoyl group, 0.42 for formyl group, 0.31 for acetoxy group, 0.18 for phenylthio group, 0.44 for acetylthio group, 0.23 for chlorine atom, 0.23 for bromine atom, 0.29 for tribromomethyl group, 0.33 for trifluoromethyl group, 0.54 for trifluoromethyl group, 0.41 for pentafluorophenyl group, 0.35 for trifluoroalkoxy group, 0.53 for N,N-trifluoromethanamino group, and 0.30 for 2,4,6-trinitrophenyl group.

Preferred among the groups represented by  $R^7$  are formyl group, acyl group, acyloxy group, carbamoyl group, alkoxycarbonyl group, aryloxycarbonyl group, cyano group, nitro group, alkylsulfinyl group, arylsulfinyl group, alkylsulfonyl group, arylsulfonyl group, alkylsulfonyl group, sulfamoyl group, halogenated alkyl group, halogenated alkyloxy group, halogenated alkylthio group, halogenated aryloxy group, aryl group substituted by two or more electrophilic groups having a Hammett's substituent constant  $\sigma_p$  of 0.15 or more, and heterocyclic group.

Further preferred among these groups are formyl group, carbamoyl group, alkoxycarbonyl group, aryloxycarbonyl group, and cyano group. Particularly preferred among these groups are cyano group, alkoxycarbonyl group, and aryloxycarbonyl group.

That is,  $R^7$  is preferably a cyano group or -COR wherein R is preferably a hydrogen atom,  $C_0-36$  amino group,  $C_1-36$ , preferably  $C_1-24$  straight-chain, branched or cyclic alkoxy group, or  $C_6-36$ , preferably  $C_6-24$  aryloxy group. These amino, alkoxy and aryloxy groups may be substituted by substituents such as substituent group A.

Alternatively,  $R^7$  is preferably a cyano group or -COR wherein R is preferably an unsubstituted, alkyl-substituted, aryl-substituted or heterocyclic group-substituted amino group (these alkyl-substituted, aryl-substituted and heterocyclic group-substituted amino groups may be further substituted by the substituent group A; the alkyl in the alkyl-substituted amino group may be a straight-chain, branched or cyclic alkyl



group; examples of such alkyl-substituted amino groups include amino, ethylamino, n-dodecylamino, anilino, 2-chloroanilino, 2-naphthylamino, 2-pyridyl-2-amino), straight-chain, branched or cyclic unsubstituted alkoxy group or alkoxy group containing substituents such as alkoxy group, alkylthio group, aryloxy group, arylthio group, alkylsulfonyl group, arylsulfonyl group, aryl group, alkoxycarbonyl group, epoxy group, cyano group and halogen atom (e.g., methoxy, ethoxy, isopropoxy, isobutoxy, n-octyloxy, n-decyloxy, n-dodecyloxy, n-hexadecyloxy, 2-ethylhexyloxy, 3,5,5-trimethylhexyloxy, 2-ethyl-4-methylpentylloxy, 2-hexyldecyloxy, 2-heptylundecyloxy, 2-octyldodecyloxy, 2,4,6-trimethylheptyloxy, 2,4,6,8-tetramethylnonyloxy, benzoyloxy, 2-phenethylloxy, 3-(1-octylphenoxy)propoxy, 3-(2,4-di-1-pentylphenoxy)propoxy, 2-(4-biphenyloxy)ethoxy, 3-dodecyloxypropoxy, 2-dodecylthioethoxy, 9,10-epoxyoctadecyloxy, dodecyloxy carbonylmethoxy, 2-(2-naphthylloxy)ethoxy, 7,7-dimethyl-2-(3',3'-dimethylbutyl)-5-methyloctyloxy, 2-methyl-cyclohexyloxy, 2-hexyl-cyclohexyloxy), unsubstituted aryloxy group or aryloxy group containing substituents (substituent group A) (e.g., phenoxy, 2-t-amyloxy, 4-dodecyloxyphenoxy).

R<sup>8</sup> and R<sup>9</sup> each independently represents a hydrogen atom or nonmetallic atomic group. In particular, R<sup>8</sup> and R<sup>9</sup> each independently represents a hydrogen atom, aryl group, heterocyclic group, alkyl group, cyano group, carboxyl group, formyl group, acyl group, carbamoyl group, alkoxycarbonyl group, aryloxy carbonyl group, acylamino group, alkoxycarbonylamino group, aryloxy carbonylamino group, sulfonylamino group, aminocarbonylamino group, sulfamoylamino group, amino group (including anilino group), alkoxy group, aryloxy group, silyloxy group, heteroalkoxy group, alkylthio group, arylthio group, heteroalkylthio group, halogen atom, hydroxyl group, nitro group, sulfamoyl group, sulfonyl group, azo group, acyloxy group, carbamoyloxy group, imido group, sulfinyl group, phosphoryl group or azolyl group. Of these nonmetallic atomic groups, those which can contain substituents may be substituted by substituents such as substituent group A.

Specific examples of R<sup>8</sup> and R<sup>9</sup> include hydrogen atom, aryl group (preferably C<sub>6-30</sub> aryl group, e.g., phenyl, m-acetylaminophenyl, p-methoxyphenyl), alkyl group (preferably C<sub>1-30</sub> alkyl group, e.g., methyl, ethyl, isopropyl, t-butyl, n-octyl, n-dodecyl), cyano group, carboxyl group, acyl group (preferably C<sub>1-30</sub> acyl group, e.g., acetyl, pivaloyl, benzoyl, furoil, 2-pyridylcarbonyl), carbamoyl group (preferably C<sub>1-30</sub> carbamoyl group, e.g., methylcarbamoyl, ethylcarbamoyl, dimethylcarbamoyl, n-octylcarbamoyl), alkoxycarbonyl group (preferably C<sub>1-30</sub> alkoxycarbonyl group, e.g., methoxycarbonyl, ethoxycarbonyl, isopropoxycarbonyl), aryloxy carbonyl group (preferably C<sub>7-30</sub> aryl group, e.g., phenoxycarbonyl, p-methoxyphenoxycarbonyl), m-chlorophenoxycarbonyl, o-methoxyphenoxycarbonyl), acylamino group (preferably C<sub>1-30</sub> alkyl carbonylamino group, e.g., formylamino, acetylamino, propionylamino, cyanoacetylamino, C<sub>7-30</sub> aryl carbonylamino group, e.g., benzoylamino, p-toluylamino, pentafluorobenzoylamino, m-methoxybenzoylamino, or C<sub>4-30</sub> heteroalkyl carbonylamino group, e.g., 2-pyridylcarbonylamino, 3-pyridylcarbonylamino, furoylamino), alkoxycarbonylamino group (preferably C<sub>2-30</sub> alkoxycarbonylamino group, e.g., methoxycarbonylamino, ethoxycarbonylamino, methoxyethoxycarbonylamino), aryloxy carbonylamino group (preferably C<sub>7-30</sub> aryloxy carbonylamino group, e.g., phenoxycarbonylamino, p-methoxyphenoxycarbonylamino, p-methylphenoxycarbonylamino, m-chlorophenoxycarbonylamino, o-chlorophenoxycarbonylamino), sulfonylamino group (preferably C<sub>1-30</sub> sulfonylamino group, e.g., methanesulfonylamino, benzenesulfonylamino, toluenesulfonylamino), aminocarbonylamino group (preferably C<sub>1-30</sub> aminocarbonylamino group, e.g., methylaminocarbonylamino, ethylaminocarbonylamino, anilino carbonylamino, dimethylaminocarbonylamino), sulfamoylamino group (preferably C<sub>1-30</sub> sulfamoylamino group, e.g., methylaminosulfonylamino, ethylaminosulfonylamino, anilinosulfonylamino), amino group (including anilino group, preferably C<sub>6-30</sub> amino group, e.g., amino, methylamino, dimethylamino, ethylamino, diethylamino, n-butylamino, anilino), alkoxy group (preferably C<sub>1-30</sub> alkoxy group, e.g., methoxy, ethoxy, isopropoxy, n-butoxy, methoxyethoxy, n-dodecyloxy), aryloxy group (preferably C<sub>6-30</sub> aryloxy group, e.g., phenoxy, m-chlorophenoxy, p-methoxyphenoxy, o-methoxyphenoxy), silyloxy group (preferably C<sub>3-30</sub> silyloxy group, e.g., trimethylsilyloxy, t-butyl dimethylsilyloxy, cetyl dimethylsilyloxy, phenyl dimethylsilyloxy), heteroalkoxy group (preferably C<sub>3-30</sub> heteroalkoxy group, e.g., tetrahydropyranyloxy, 3-pyridyloxy, 2-(1,3-benzimidazolyl)oxy), alkylthio group (preferably C<sub>1-30</sub> alkylthio group, e.g., methylthio, ethylthio, n-butylthio, t-butylthio), arylthio group (preferably C<sub>6-30</sub> arylthio group, e.g., phenylthio), heteroalkylthio group (preferably C<sub>3-30</sub> heteroalkylthio group, e.g., 2-pyridylthio, 2-(1,3-benzoxazolyl)thio, 1-hexadecyl-1,2,3,4-tetrazolyl-5-thio, 1-(3-N-octadecyl carbamoyl)phenyl-1,2,3,4-tetrazolyl-5-thio), heterocyclic group (preferably C<sub>3-30</sub> heterocyclic group, e.g., 2-benzoxazolyl, 2-benzothiazolyl, 1-phenyl-2-benzimidazolyl, 5-chloro-1-tetrazolyl, 1-pyrrolyl, 2-furanyl, 2-pyridyl, 3-pyridyl), halogen atom (e.g., fluorine, chlorine, bromine), hydroxyl group, nitro group, sulfamoyl group (preferably C<sub>6-30</sub> sulfamoyl group, e.g., methylsulfamoyl, dimethylsulfamoyl), sulfonyl group (preferably C<sub>1-30</sub> sulfonyl group, e.g., methanesulfonyl, benzenesulfonyl, toluenesulfonyl), azo group (preferably C<sub>3-30</sub> azo group, e.g., p-nitrophenylazo), acyloxy group (preferably C<sub>1-30</sub> acyloxy group, e.g., formyloxy, acetyloxy, benzoyloxy), carbamoyloxy group (preferably C<sub>1-30</sub> aryl group, e.g., methylcar-

bamoyloxy, diethylcarbamoyloxy), imido group (preferably C<sub>4-30</sub> imido group, e.g., succinimido, phthalimido), sulfinyl group (preferably C<sub>1-30</sub> sulfinyl group, e.g., diethylaminosulfinyl), phosphoryl group (preferably C<sub>0-30</sub> phosphoryl group, e.g., diaminophosphoryl), and azolyl group (preferably C<sub>2-30</sub> azolyl group, e.g., 3-pyrazolyl).

5 Among these specific examples of R<sup>8</sup>,  $\sigma_p$  values other than those described with reference to R<sup>7</sup> are 0.00 for hydrogen atom, -0.17 for methyl group, -0.15 for ethyl group, -0.01 for phenyl group, 0.00 for acetylamino group, 0.03 for methanesulfonamido group, -0.15 for carbonylamino group, etc.

R<sup>8</sup> preferably represents an electrophilic group having a Hammett's substituent constant  $\sigma_p$  of 0.15 or more, i.e., it is synonymous with R<sup>7</sup>. Particularly preferred examples of R<sup>8</sup> include cyano group, formyl group, carbamoyl group, alkoxy carbonyl group, and aryloxy carbonyl group. That is, R<sup>8</sup> is preferably a  
10 cyano group or -COR wherein R is the same as defined above for R<sup>7</sup>. More preferred among these groups are cyano group, alkoxy carbonyl group, and aryloxy carbonyl group. Particularly preferred among these groups are alkoxy carbonyl group and aryloxy carbonyl group.

In the present invention, the sum of  $\sigma_p$  values of R<sup>7</sup> and R<sup>8</sup> is 0.65 or more. Any combination of R<sup>7</sup> and  
15 R<sup>8</sup> is possible so far as R<sup>7</sup> has a  $\sigma_p$  value of 0.15 or more. Examples of such a combination will be set forth below, but the present invention should not be construed as being limited thereto.

| R <sup>7</sup>                                |      | R <sup>8</sup>                                |       | Sum  |
|---|------|---|-------|------|
| CN  | 0.66 | CN  | 0.66  | 1.32 |
| CN  | 0.66 | COCH <sub>3</sub>                             | 0.50  | 1.16 |
| CN  | 0.66 | CO <sub>2</sub> CH <sub>3</sub>               | 0.45  | 1.11 |
| CN  | 0.66 | CONH <sub>2</sub>                             | 0.38  | 1.02 |
| CONH <sub>2</sub>                             | 0.38 | CONH <sub>2</sub>                             | 0.38  | 0.72 |
| CONH <sub>2</sub>                             | 0.38 | CN  | 0.66  | 1.02 |
| CONH <sub>2</sub>                             | 0.38 | CO <sub>2</sub> CH <sub>3</sub>               | 0.50  | 0.88 |
| COCH <sub>3</sub>                             | 0.50 | CN  | 0.66  | 1.16 |
| COCH <sub>3</sub>                             | 0.50 | COCH <sub>3</sub>                             | 0.50  | 1.00 |
| NO <sub>2</sub>                               | 0.78 | C <sub>6</sub> H <sub>5</sub>                 | -0.01 | 0.77 |
| CN  | 0.66 | CO <sub>2</sub> C <sub>6</sub> H <sub>5</sub> | 0.44  | 1.10 |
| CO <sub>2</sub> C <sub>6</sub> H <sub>5</sub> | 0.44 | CHO   | 0.42  | 0.86 |
| CN  | 0.66 | CONHCH <sub>3</sub>                           | 0.36  | 1.02 |
| CN  | 0.66 | CF <sub>3</sub>                               | 0.54  | 1.20 |

35 Preferred examples of R<sup>9</sup> include aryl group, heterocyclic group, and alkyl group. Suitable among these groups is aryl group, preferably C<sub>6-36</sub>, more preferably C<sub>6-30</sub> aryl group. The aryl group is preferably an unsubstituted aryl group or an aryl group containing substituents (substituent group A) or which may be condensed (e.g., phenyl, 3-nitrophenyl, 4-nitrophenyl, 4-cyanophenyl, 3,4-dicyanophenyl, 3,4-dimethoxycarbonylphenyl, 3-(2-octyloxy-5-t-octyl)phenylsulfonaminophenyl, 3,5-dichlorophenyl, 4-[1-(2,4-di-t-amylphenoxy)propanoylamino]phenyl, 4-(2-hexyldecyloxy)phenyl, 2-(2-hexyldecyloxy)phenyl, and 3-(2,4-di-t-amylphenoxyacetylamino)phenyl).

Preferred examples of substituents to be contained in the substituted aryl group include nitro group, halogen atom, cyano group, acylamino group, and sulfonamido group. Particularly preferred among these  
40 substituents is chlorine atom.

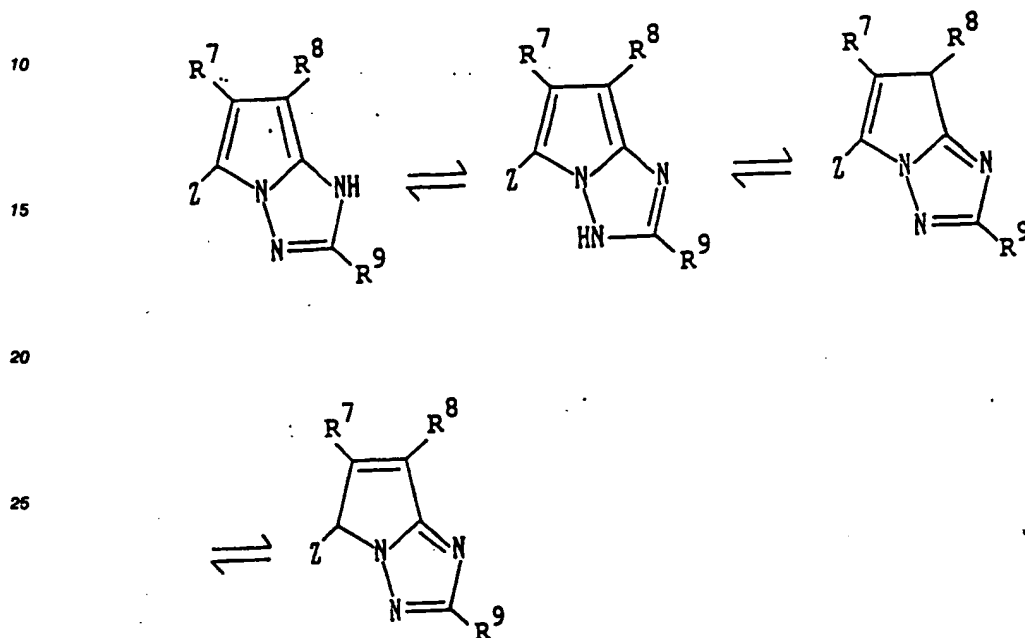
45 Z preferably represents a hydrogen atom, halogen atom, C<sub>6-36</sub>, preferably C<sub>6-24</sub> arylthio group, C<sub>1-36</sub>, preferably C<sub>1-24</sub> arylsulfinyl group, C<sub>1-36</sub>, preferably C<sub>1-24</sub> heterocyclic thio group, or nitroso group. These arylthio group, arylsulfinyl group and heterocyclic thio group may be substituted by the substituent group A.

50 Preferred examples of Z include hydrogen atom, halogen atom (e.g., fluorine atom, chlorine atom, bromine atom), unsubstituted arylthio group or arylthio group containing substituents such as halogen atom, alkyl group, alkoxy group, cyano group, aryloxy carbonyl group, alkoxy carbonyl group, ureido group, alkoxy carbonylamino group, acylamino group and carboxyl group (e.g., 2-(n-butoxy)-5-(t-octyloxy)-phenylthio, 2-(t-amylcarbonylamino)phenylthio, 2-(phenoxycarbonylamino)phenylthio, 2-(phenoxycarbonyl)-phenylthio, 2-(3,3-dimethylureido)phenylthio, pentafluorophenylthio, pentachlorophenylthio, 1,3,5-triisopropylphenylthio), unsubstituted arylsulfinyl group or arylsulfinyl group containing substituents such as halogen  
55 atom, alkyl group, alkoxy group, cyano group, alkoxy carbonyl group and carboxyl group (e.g., 2-(n-butoxy)-5-(t-octyloxy)phenylsulfinyl, 2-(t-amylcarbonylamino)phenylsulfinyl, 2-(phenoxycarbonylamino)phenylsulfinyl, 2-(phenoxycarbonyl)phenylsulfinyl, 2-(3,3-dimethylureido)phenylsulfinyl, pentafluorophenylsulfinyl, pentach-

lorophenylsulfinyl, 1,3,5-trisopropylphenylsulfinyl), unsubstituted heterocyclic thio group or heterocyclic thio group containing substituents such as halogen atom, alkyl group, alkoxy group, cyano group, alkoxycarbonyl group, carboxyl group and nitro group (e.g., pyrazolylthio, 5-nitro-2-pyridylthio) or nitroso group.

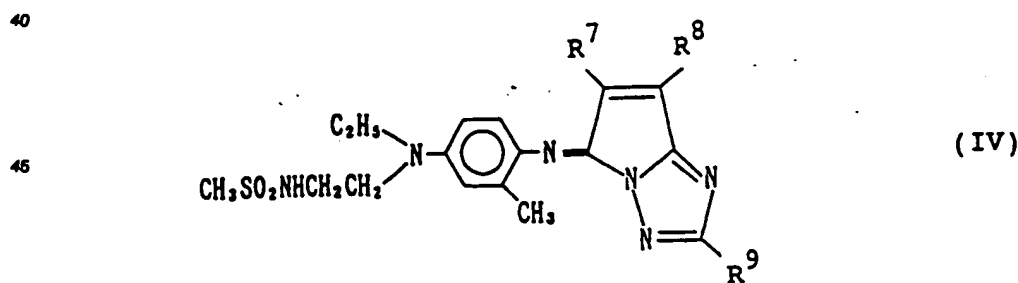
Preferred among these groups are hydrogen atom, arylthio group, and arylsulfinyl group.

The compound represented by formula (III) also indicates various compounds in equilibrium as shown below:

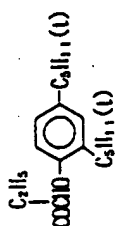
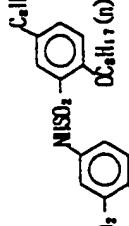
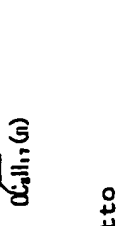



Specific examples of the compound of the present invention will be set forth below, but the present invention should not be construed as being limited thereto.

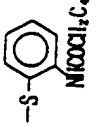
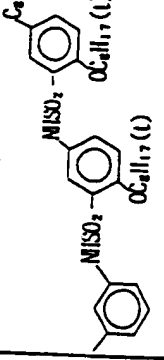
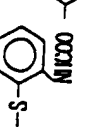
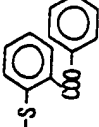
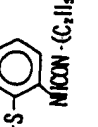

Firstly, specific examples of the compounds represented by formulae (I) and (III) will be given. In the structural formulae shown below, (t)C<sub>5</sub>H<sub>11</sub> indicates -C(CH<sub>3</sub>)<sub>2</sub>C<sub>2</sub>H<sub>5</sub>, and (t)C<sub>8</sub>H<sub>17</sub> indicates -C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>. M<sup>\*</sup> indicates the value (M<sup>\*</sup>) of the master peak of mass spectrum. λ<sub>max</sub>(nm) indicates the maximum absorption wavelength of ethyl acetate solution of a compound represented by formula (IV) when derived from the compound represented by formula (I):

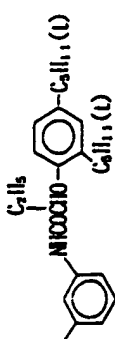
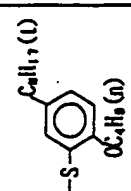


Some examples of the compound represented by formula (III) will be shown with their melting points (m.p.).

| Comp. No. | R <sup>6</sup> | M <sup>4</sup> | R <sup>7</sup>   | Z  | R <sup>5</sup>  | ( $\mu$ ), $\lambda_{max}$ | m. p. | $\lambda_{max}$ (nm) |
|-----------|----------------|----------------|--|----|---|----------------------------|-------|----------------------|
| III-1     | CN             | 583            | COOCH <sub>3</sub>   | H  |  | 104 °C                     | 616   |                      |
| III-2     | CN             | 1077           | COOCH <sub>2</sub> CH(C <sub>6</sub> H <sub>5</sub> )C <sub>6</sub> H <sub>5</sub><br> <br>C <sub>6</sub> H <sub>5</sub> | Cl |  | —                          | —     | 621                  |
| III-3     | CN             | 1021           | COOCH <sub>2</sub> CH <sub>2</sub> (i)   | Cl | ditto   | —                          | —     | 621                  |
| III-4     | CN             | 1021           | COOCH <sub>2</sub> CH <sub>2</sub> (n)   | Cl | ditto   | —                          | —     | 620                  |
| III-5     | CN             | 1036           |   | H  | ditto   | —                          | —     | —                    |
| III-6     | CN             | 1070           |                                        | Cl | ditto   | —                          | —     | —                    |
| III-7     | CN             | 1007           | COOCH <sub>2</sub> CH <sub>2</sub> (i)   | Cl | ditto   | —                          | —     | —                    |

| Comp. No. | R <sup>a</sup> | M'   | R <sup>z</sup>  | Z  | R <sup>9</sup> | m. p. | $\lambda_{max}$ (nm) |
|-----------|----------------|------|---|----|----------------|-------|----------------------|
| III-8     | CN             | 973  | $COOC_2H_5(i)$  | II |                | —     | —                    |
| III-9     | CN             | 1237 | $COOCH_3$   |    | ditto          | 130°C | —                    |
| III-10    | CN             | 989  | $COOCH_2CH_2OCH_3$                                      | II | ditto          | —     | —                    |
| III-11    | CN             | 987  | $COOC_4H_9(i)$  | II | ditto          | 20°C  | —                    |
| III-12    | CN             | 1043 | $COOCH_2CH_2C_4H_9(n)$<br>C <sub>2</sub> H <sub>5</sub> | II | ditto          | 17°C  | —                    |
| III-13    | CN             | 987  | $COOC_4H_9(n)$  | II | ditto          | —     | —                    |
| III-14    | CN             | 1279 | $COOC_4H_9(n)$  |    | ditto          | —     | —                    |

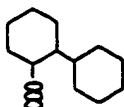
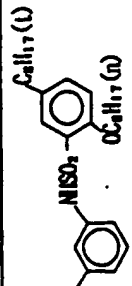

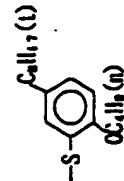
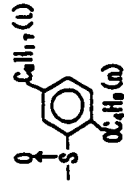
| Comp. No. | R <sup>u</sup> | M <sup>+</sup> | R <sup>v</sup>                       | Z  | R <sup>9</sup>  | (m)<br>λ <sub>max</sub> | m.p.        | λ <sub>mix</sub> (nm) |
|-----------|----------------|----------------|--------------------------------------|--|---|-------------------------|-------------|-----------------------|
| III-15    | CN             | 1208           | COOC <sub>4</sub> H <sub>9</sub> (i) |    |  | (m)<br>λ <sub>max</sub> | m.p.        | λ <sub>mix</sub> (nm) |
| III-16    | CN             | 1230           | COOC <sub>4</sub> H <sub>9</sub> (i) |    | ditto   |                         | —           | —                     |
| III-17    | CN             | 1215           | COOC <sub>4</sub> H <sub>9</sub> (i) |  | ditto   |                         | —           | —                     |
| III-18    | CN             | 1208           | COOC <sub>4</sub> H <sub>9</sub> (i) |  | ditto   |                         | 194 ~ 197°C | —                     |
| III-19    | CN             | 1141           | COOC <sub>4</sub> H <sub>9</sub> (i) |  | ditto   |                         | —           | —                     |

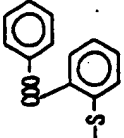
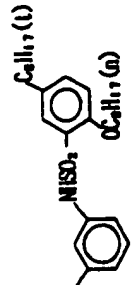
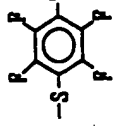
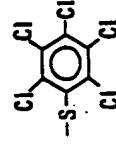
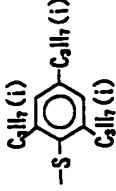
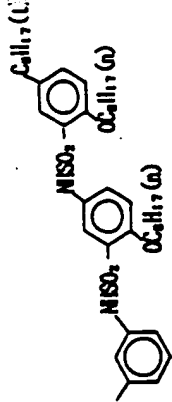
| Comp. No. | R <sup>6</sup> | M <sup>*</sup> | R <sup>7</sup>     | Z   | R <sup>9</sup>  | m.p. °C | $\lambda_{\text{max}}$ (nm) |
|-----------|----------------|----------------|--------------------|---|---|---------|-----------------------------|
| III-20    | CN             | 018            | COOCH <sub>3</sub> | Cl  |  | 146 °C  | —                           |
| III-21    | CN             | 870            | COOCH <sub>3</sub> |  | ditto   | 103 °C  | —                           |

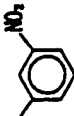
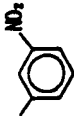

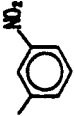
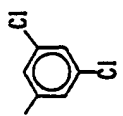

| Comp. No. | R <sup>6</sup> | M <sup>+</sup> | R <sup>7</sup> | R <sup>9</sup> | $\mu$ (D) | $\lambda_{max}$ (nm) |
|-----------|----------------|----------------|----------------|----------------|-----------|----------------------|
| III-22    | $COOC_2H_5$    | 959            | CN             |                | —         | 0 2 8                |
| III-23    | $COOC_2H_5$    | 1043           | CN             | ditto          | 182 °C    | —                    |
| III-24    | $COOC_2H_5$    | 987            | CN             | ditto          | 157 °C    | 0 3 0                |
| III-25    | $COOC_2H_5$    | 545            | CN             |                | 97 °C     | 0 2 9                |
| III-26    | $COOC_2H_5$    | 597            | CN             |                | 114 °C    | 0 2 5                |

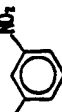
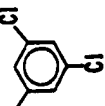
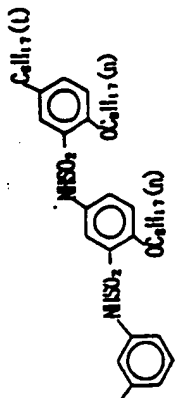
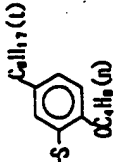
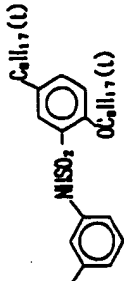




| Comp. No. | R <sup>6</sup>  | M <sup>+</sup> | R <sup>7</sup> | Z  | R <sup>9</sup> | m.p.    | $\lambda_{\text{max}}$ (nm) |
|-----------|---|----------------|----------------|----|----------------|---------|-----------------------------|
| III-27    | $\text{Cl}_3$<br>$\text{ClCH}_2\text{C}_6\text{H}_4$ (l)<br>$\text{COOCH}_2\text{Cl}$<br>$\text{Cl}_3$<br>$\text{CH}_2-\text{CHCH}_2\text{C}_6\text{H}_4$ (l) | 822            | CN             | II |                | 78 °C   | 0 2 7                       |
| III-28    | $\text{COOC}_2\text{H}_5$<br>$\text{Cl}_3$  | 675            | CN             | II |                | —       | 0 2 4                       |
| III-29    | $\text{COOC}_2\text{H}_5$<br>$\text{Cl}_3$  | 675            | CN             | II |                | 240 °C  | 0 2 9                       |
| III-30    | $\text{Cl}_3$<br>$\text{COOCH}_2\text{CHClCH}_2\text{C}_6\text{H}_4$ (l)<br>$\text{Cl}_3$<br>$\text{CH}_2\text{CH}_2\text{CHClCH}_2\text{C}_6\text{H}_4$ (l)  | 900            | CN             | II | ditto          | —       | 0 4 0                       |
| III-31    | $\text{COOC}_1\text{H}_{13}$ (n)<br>$\text{Cl}_3$   | 844            | CN             | II | ditto          | 180 °C  | —                           |
| III-32    |   | 743            | CN             | II | ditto          | >250 °C | —                           |

| Comp. No. | R <sup>6</sup>  | M <sup>1</sup> | R <sup>7</sup> | Z   | R <sup>8</sup>  | $\lambda_{\text{max}}$ (nm) | M. P.  | $\lambda_{\text{max}}$ (nm) |
|-----------|---|----------------|----------------|---|---|-----------------------------|--------|-----------------------------|
| III-33    |  | 812            | CN             | II  |  | —                           | 144 °C | —                           |
| III-34    |  | 816            | CN             | II  | ditto   | —                           | 123 °C | —                           |
| III-35    | $\text{COOCH}_2\text{CH}_2\text{-(CF}_2\text{)}_6\text{F}$                          | 983            | CN             | II  | ditto   | 0.38                        | 191 °C | 0.38                        |
| III-36    | $\text{COOCH}_2\text{-(CF}_2\text{)}_7\text{H}$                                     | 881            | CN             | II  | ditto   | 0.40                        | 101 °C | 0.40                        |
| III-37    | $\text{COOC}_2\text{H}_5$   | 938            | CN             |   | ditto   | —                           | 181 °C | —                           |
| III-38    | $\text{COOC}_2\text{H}_5$   | 984            | CN             |  | ditto   | —                           | 142 °C | —                           |

| Comp. No. | R <sup>6</sup>                   | M <sup>4</sup> | R <sup>7</sup>     | Z  | R <sup>9</sup>  | m.p.         | $\lambda_{max}$ (nm) |
|-----------|----------------------------------|----------------|--------------------|--|---|--------------|----------------------|
| III-39    | COOC <sub>2</sub> H <sub>5</sub> | 815            | CN                 |    |    | 228 °C       | —                    |
| III-40    | COOC <sub>2</sub> H <sub>5</sub> | 817            | CN                 |    | ditto   | 108 ~ 110 °C | —                    |
| III-41    | COOC <sub>2</sub> H <sub>5</sub> | 900            | CN                 |    | ditto   | —            | —                    |
| III-42    | COOC <sub>2</sub> H <sub>5</sub> | 909            | CN                 |  | ditto   | 104 ~ 107 °C | —                    |
| III-43    | CN                               | 944            | COOCH <sub>3</sub> | II   |  | 212 °C       | 0.20                 |

| Comp. No. | R <sup>6</sup>                   | M <sup>+</sup> | R <sup>7</sup>     | Z  | R <sup>8</sup>  | $\lambda_{\text{max}}$ (nm) | m.p.   | $\lambda_{\text{max}}$ (nm) |
|-----------|----------------------------------|----------------|--------------------|----|---|-----------------------------|--------|-----------------------------|
| III-44    | CN                               | 278            | CN                 | II |    | —                           | —      | —                           |
| III-45    | COOC <sub>2</sub> H <sub>5</sub> | 325            | CN                 | II |    | —                           | —      | 629                         |
| III-46    | COOC <sub>2</sub> H <sub>5</sub> | 337            | CN                 | II |    | —                           | 250 °C | —                           |
| III-47    | CN                               | 311            | COOCH <sub>3</sub> | II |   | —                           | —      | —                           |
| III-48    | COOC <sub>2</sub> H <sub>5</sub> | 348            | CN                 | II |  | —                           | —      | 628                         |
| III-49    | COOC <sub>2</sub> H <sub>5</sub> | 325            | CN                 | H  |  | —                           | —      | —                           |

| Comp. No. | R <sup>a</sup>  | M <sup>+</sup> | R <sup>7</sup>  | Z   | R <sup>8</sup>  | m.p.        | $\lambda_{max}$ (nm) |
|-----------|---|----------------|---|---|---|-------------|----------------------|
| III-50    | CNII <sub>2</sub>   | 298            | CN  | II  |    | —           | 011                  |
| III-51    | CN  | 334            | COOCl <sub>2</sub>  | II  |    | 205 ~ 207°C | 010                  |
| III-52    | CN  | 1023           | COOCl <sub>2</sub> Cl <sub>2</sub> COCl <sub>2</sub>                                    | Cl  |    | 143 ~ 145°C | 035                  |
| III-53    | CN  | 1336           | COOCl <sub>2</sub> ClC <sub>4</sub> H <sub>9</sub> (n)<br>C <sub>6</sub> H <sub>5</sub> |  | ditto   | —           | —                    |
| III-54    | COOC <sub>4</sub> H <sub>9</sub>  | 710            | CN  | Cl  |  | —           | —                    |
| III-55    | CNII-  | 378            | CN  | II  |  | —           | 011                  |

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| Comp. No. | R <sup>6</sup> | M <sup>+</sup> | R <sup>7</sup> | Z  | R <sup>8</sup> | m.p. | $\lambda_{max}$ |
|-----------|----------------|----------------|----------------|----|----------------|------|-----------------|
| III-56    |                | 280            | CN             | II |                | —    | 621             |
| III-57    |                | 504            | CN             | H  |                | —    | 624             |
| III-58    |                | 506            | CN             | II |                | —    | —               |
| III-59    |                | 808            | CN             | II |                | —    | 644             |

45 Specific examples of the compounds represented by formulae (I) and (II) will be given below. In the structural formulae shown below, Ph represents a phenyl group.

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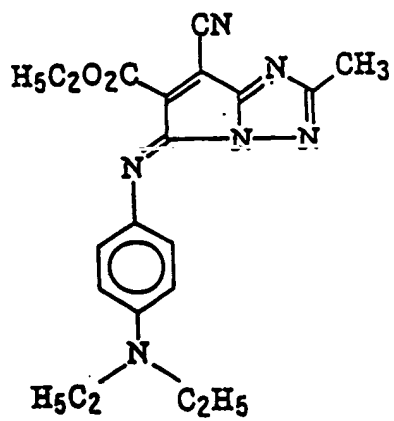
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(I-1)

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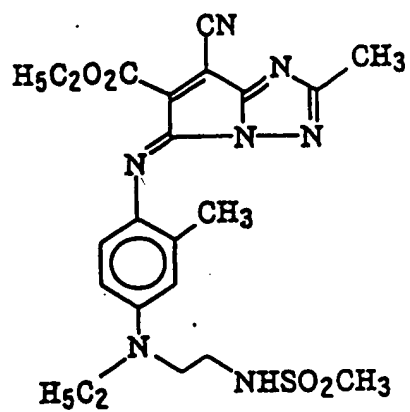
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(I-2)

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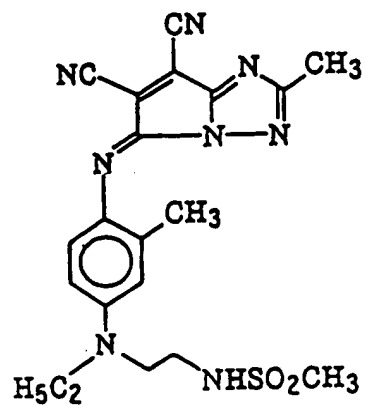
(I-3)

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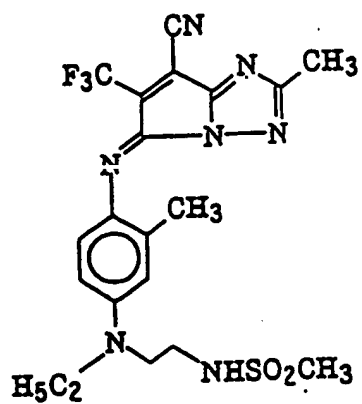
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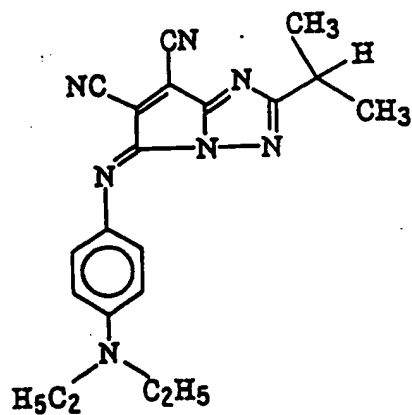
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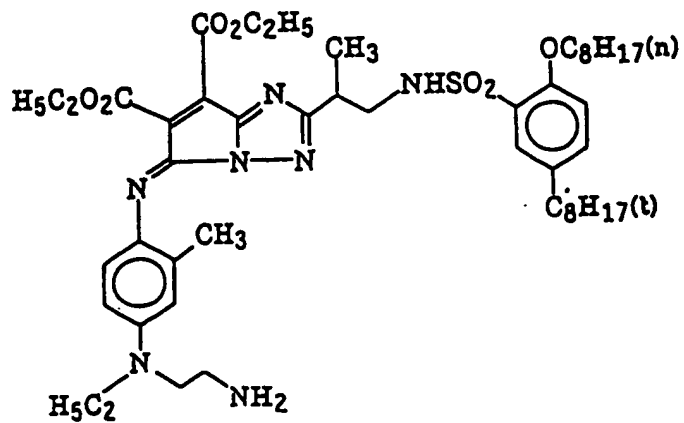
(I-4)



(I-5)

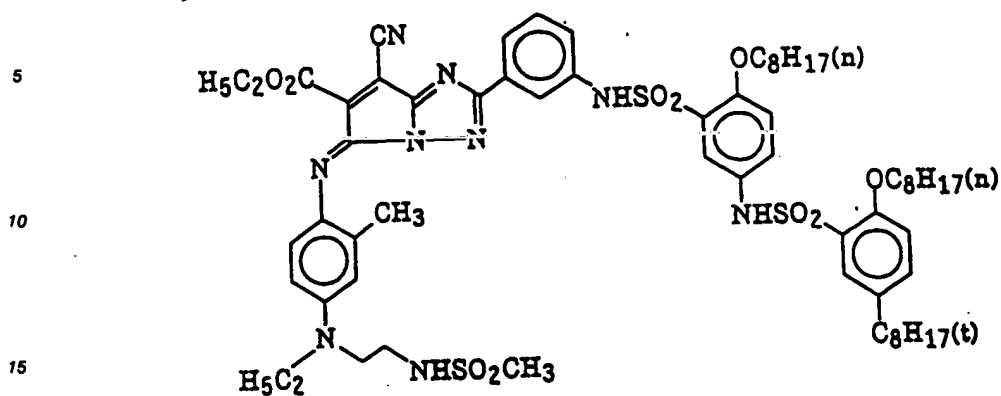


(I-6)

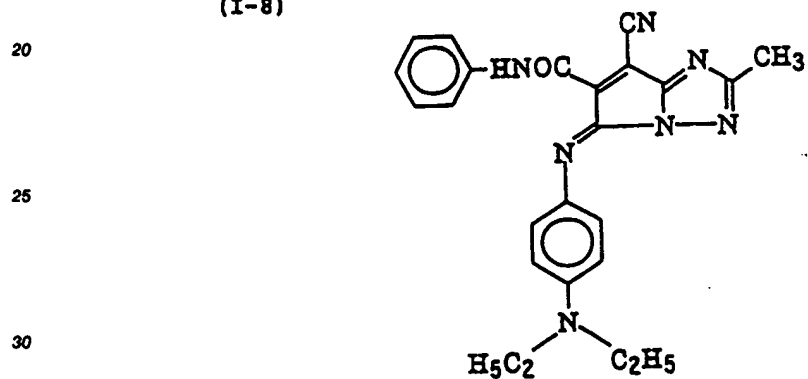




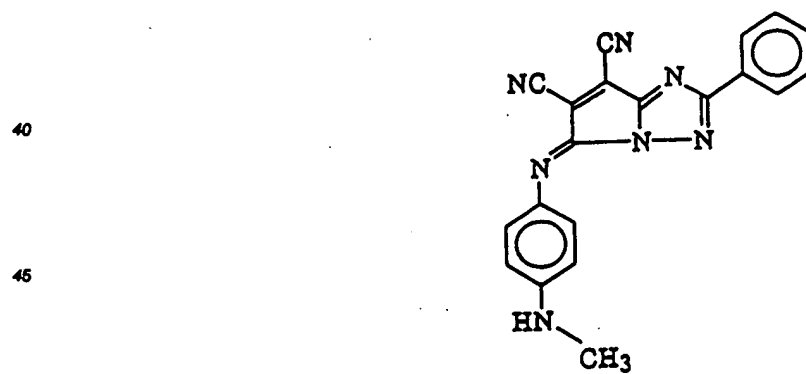
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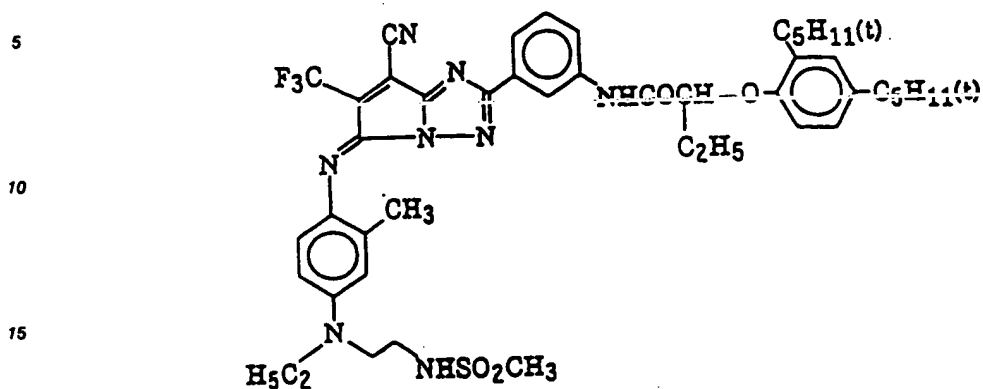
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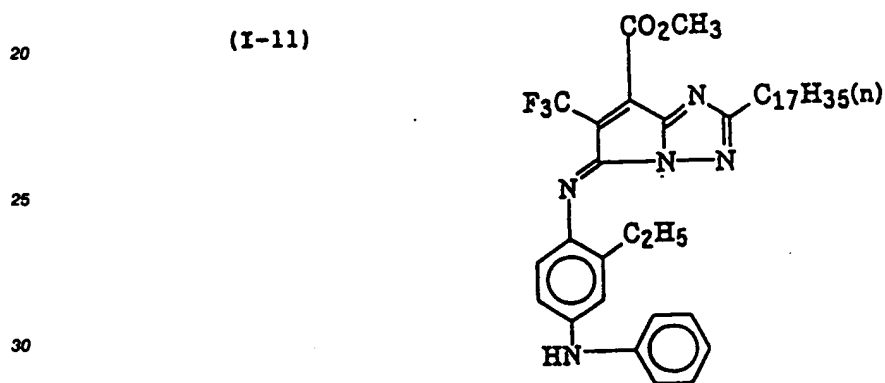
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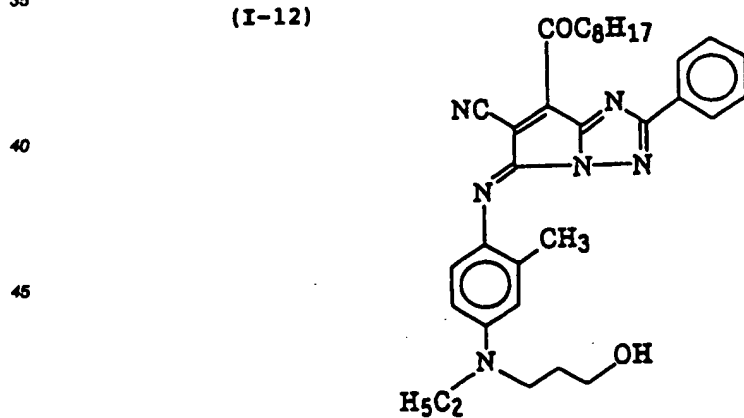
(I-10)



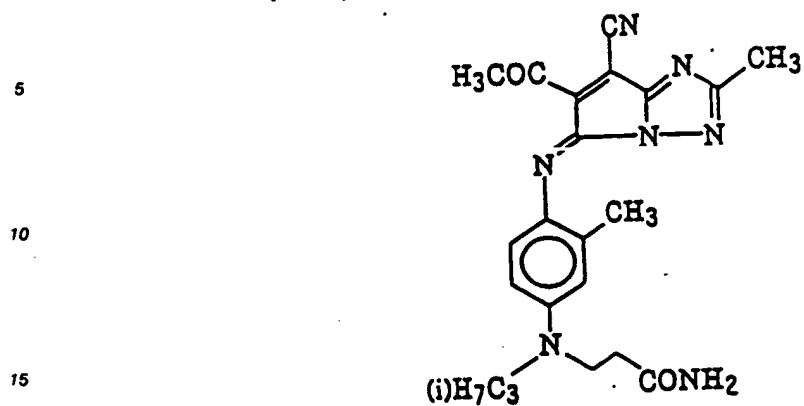
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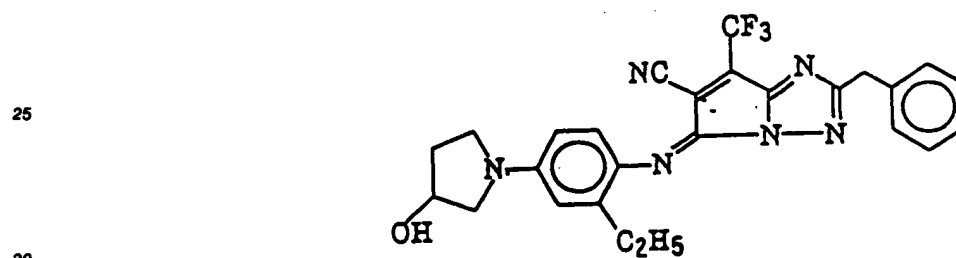
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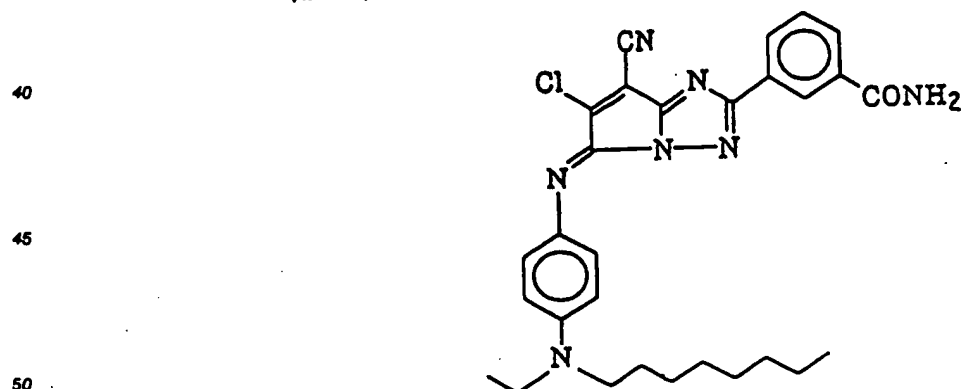
(I-13)



(I-14)



(I-15)



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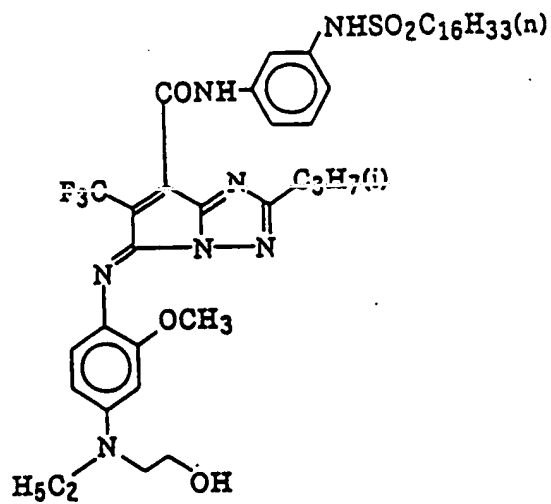
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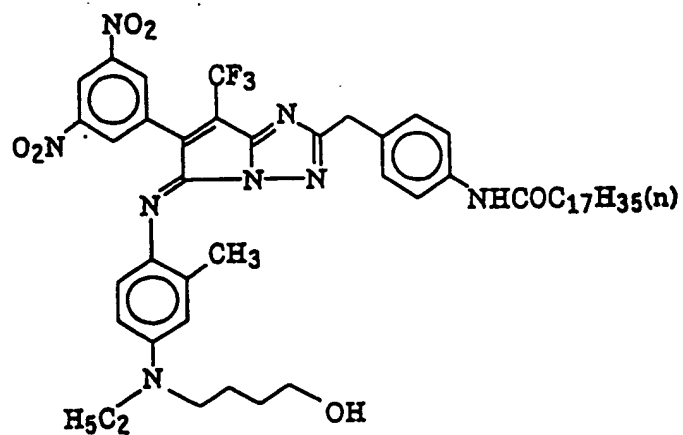
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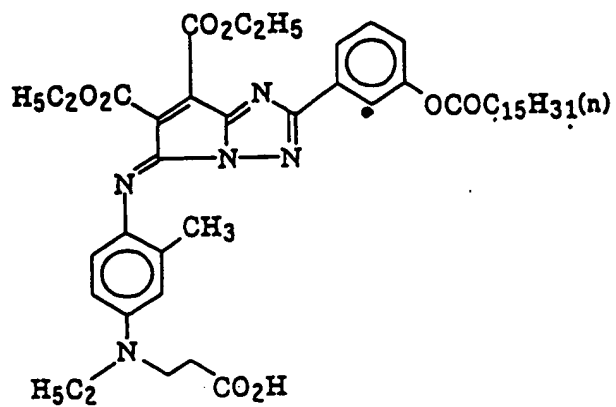
(I-19)



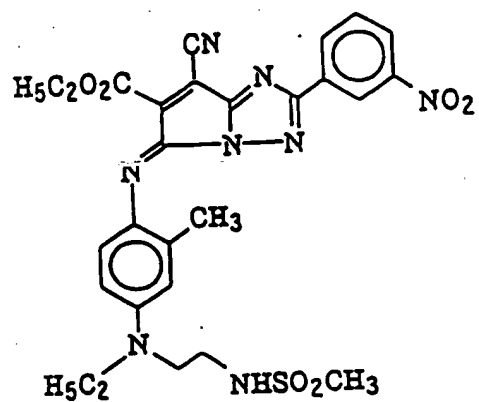
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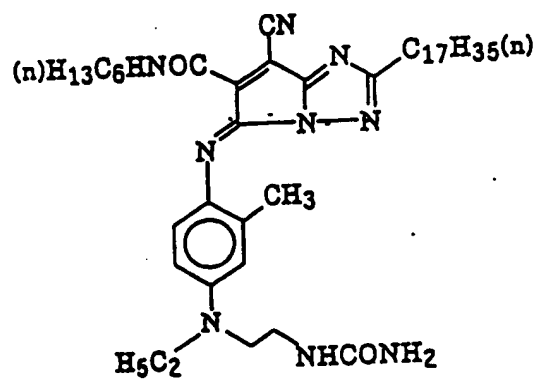
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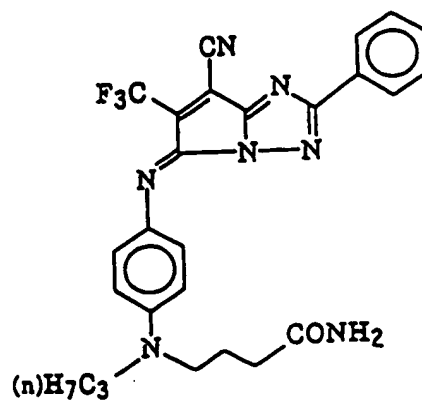
(I-22)



(I-23)



(I-24)

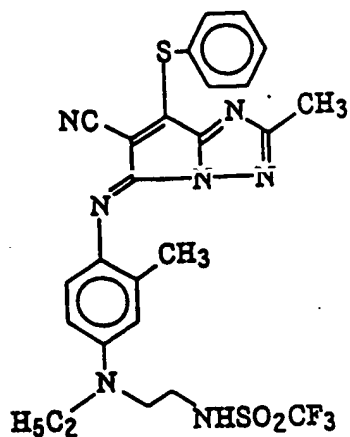


(I-25)

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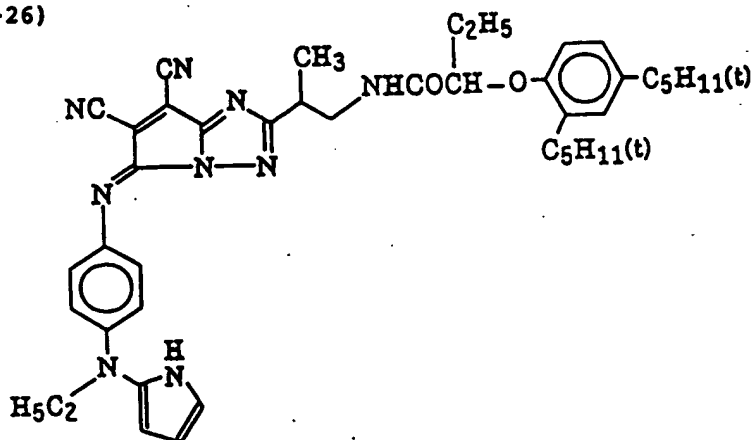
(I-26)

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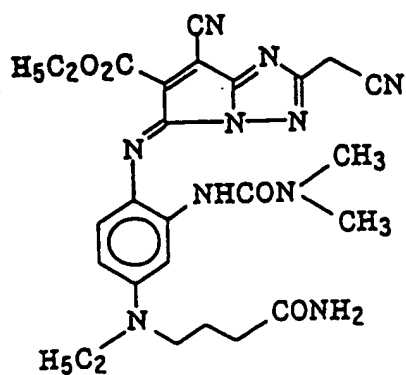
(I-27)

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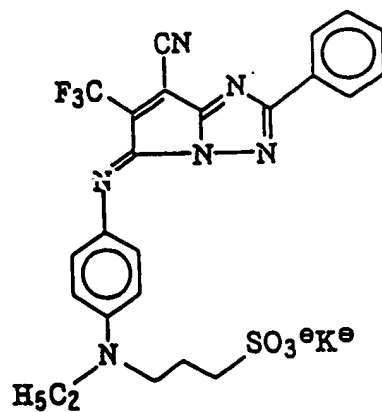


(I-28)

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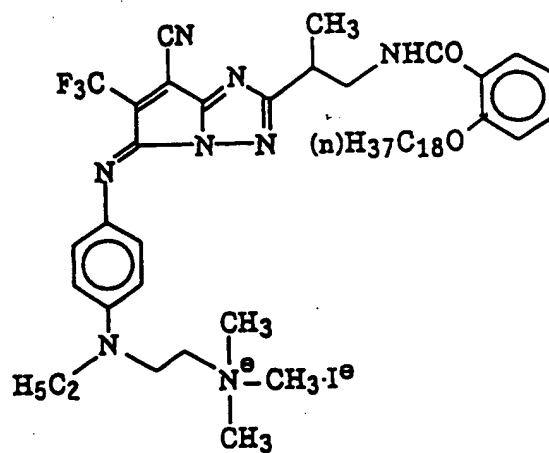
(I-29)

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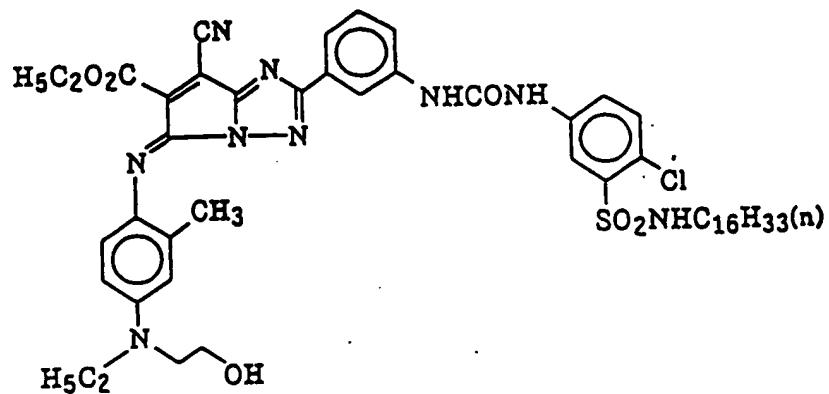
(I-30)

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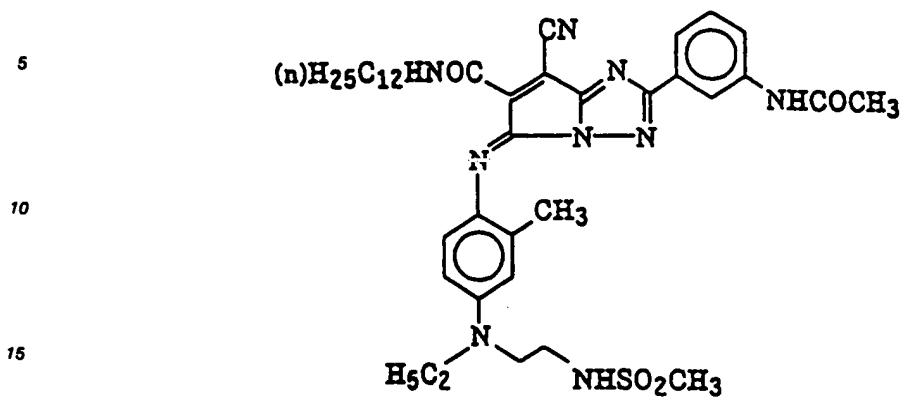
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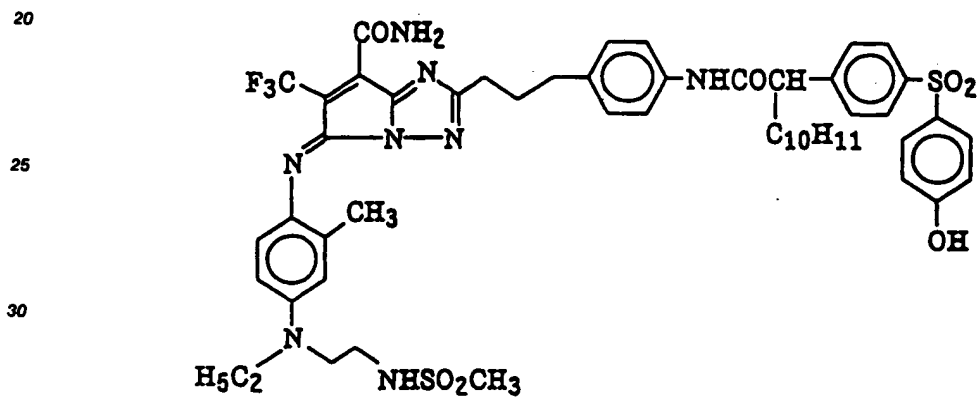




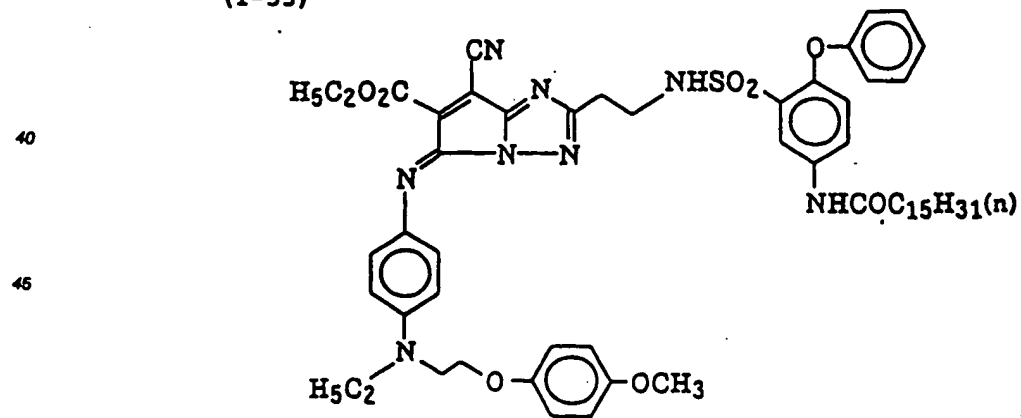
(I-31)



(I-32)

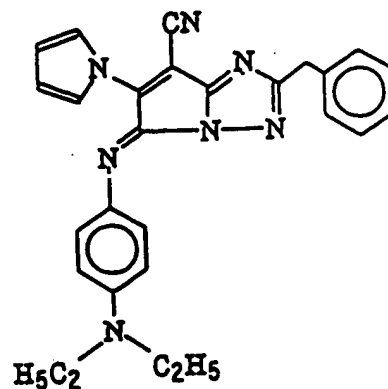


(I-33)

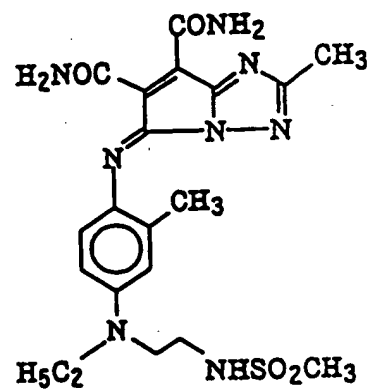


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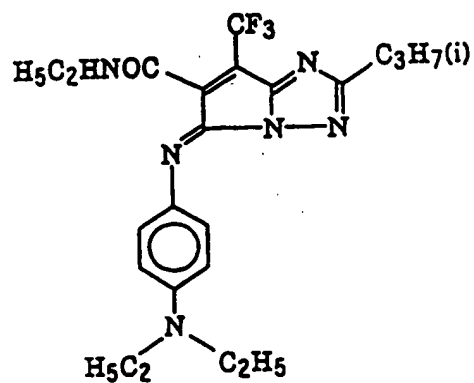
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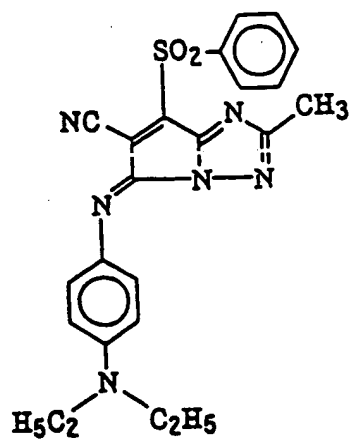
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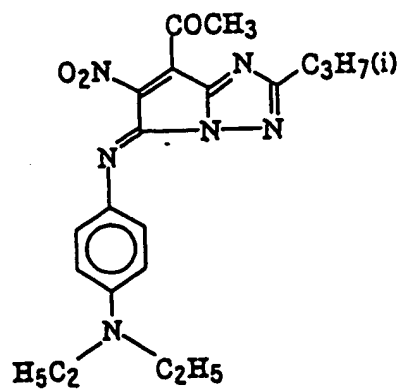
(I-36)



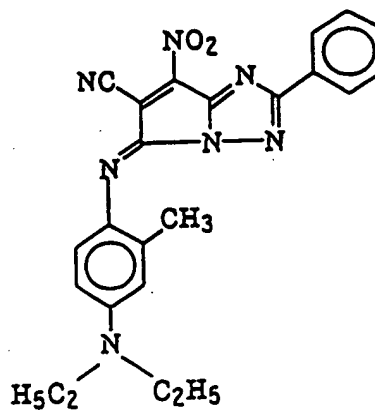
(I-37)



(I-38)



(I-39)

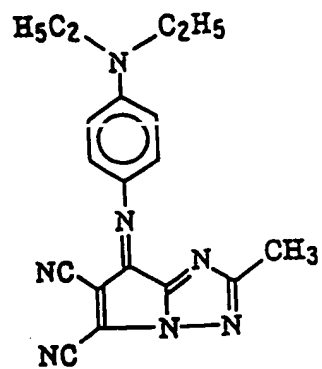


(II-1)

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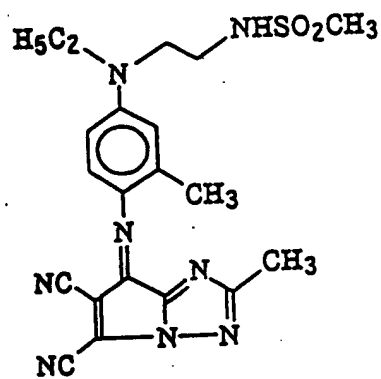


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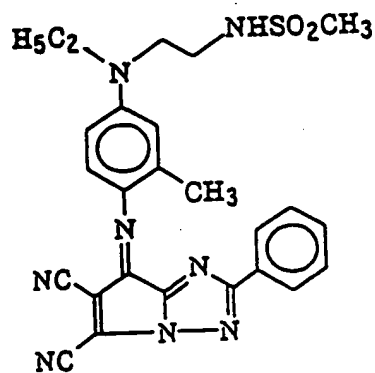
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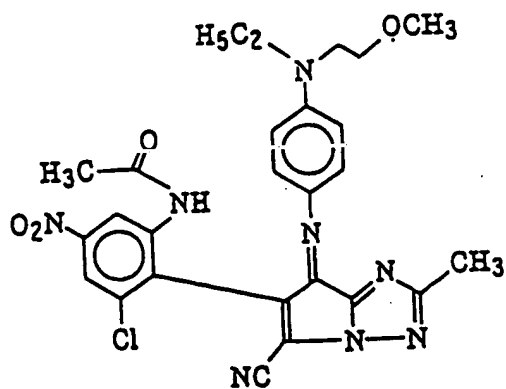
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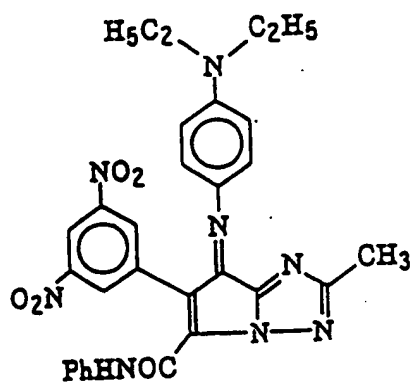
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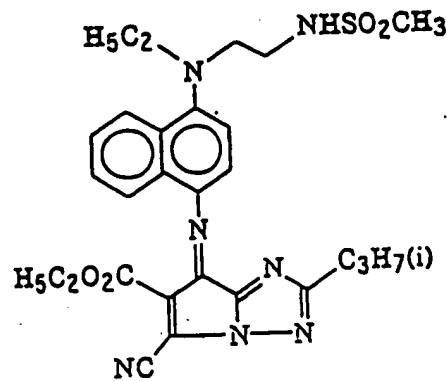
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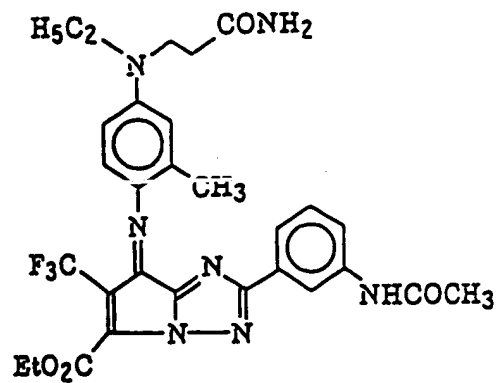
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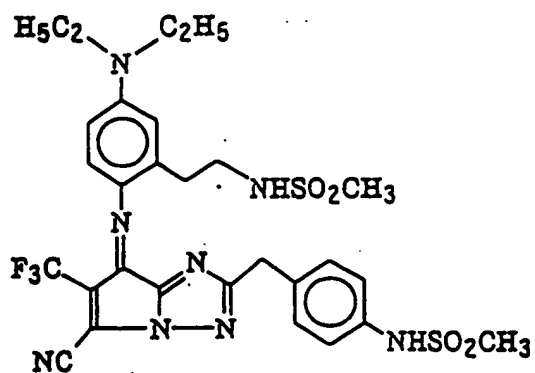
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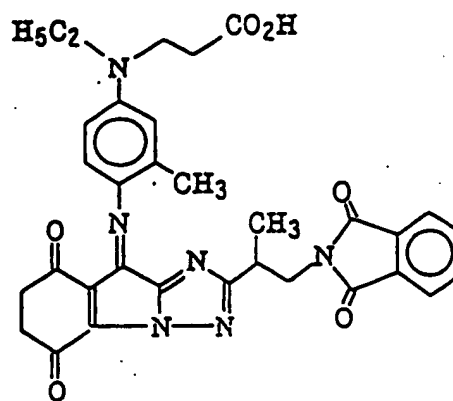
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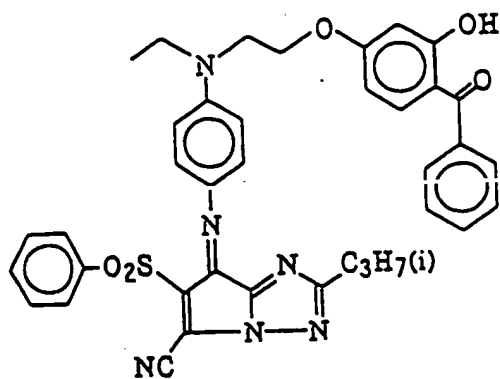
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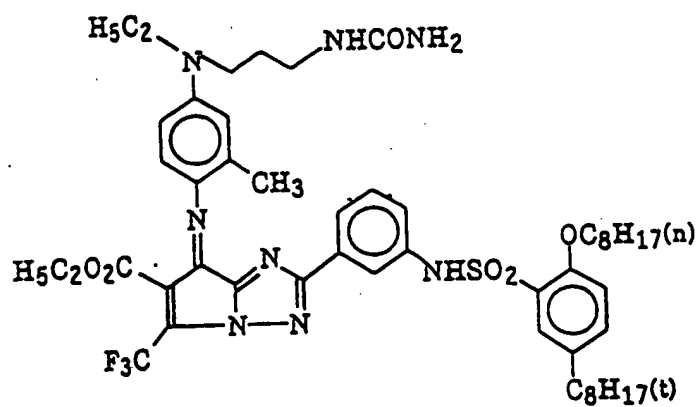
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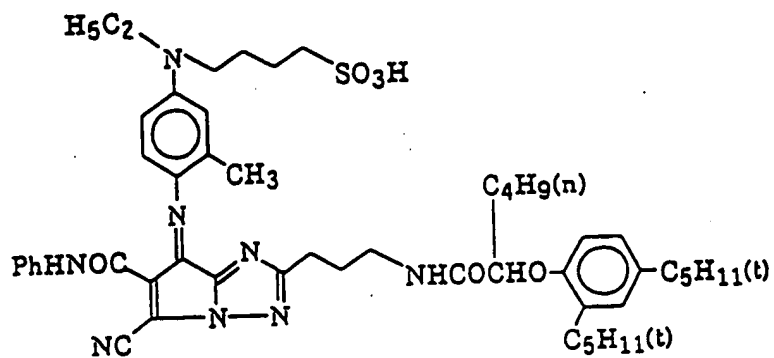
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(II-11)



(II-12)

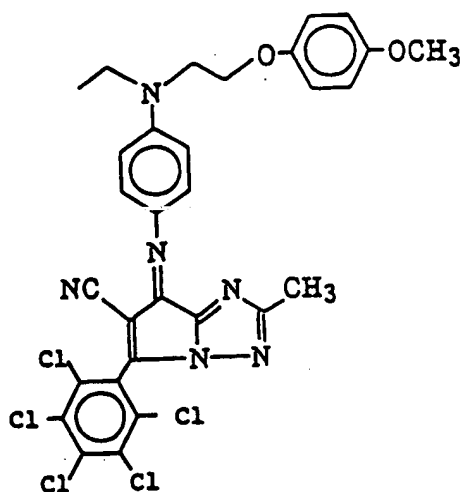


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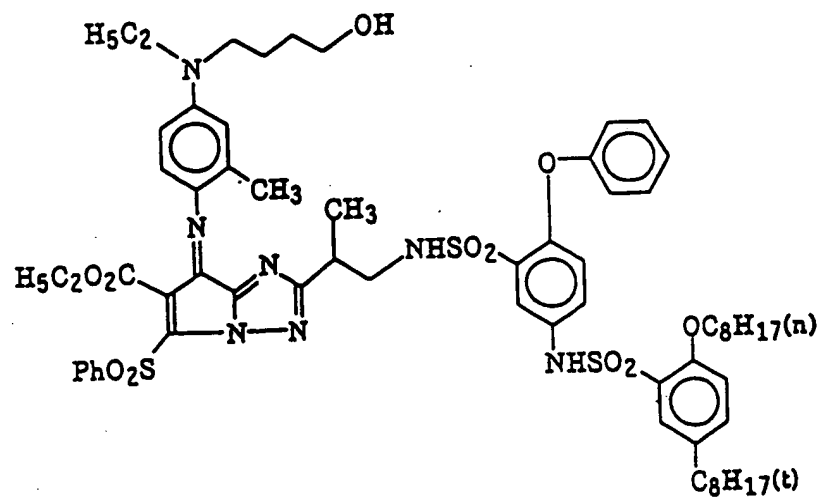
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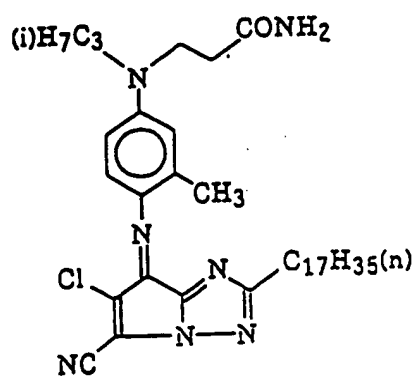
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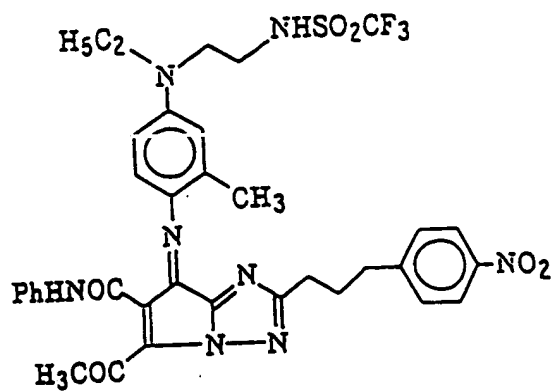
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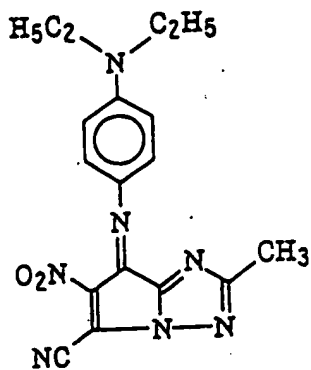




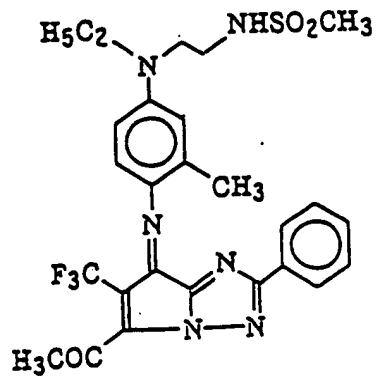
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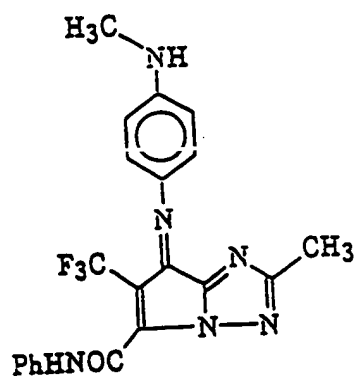
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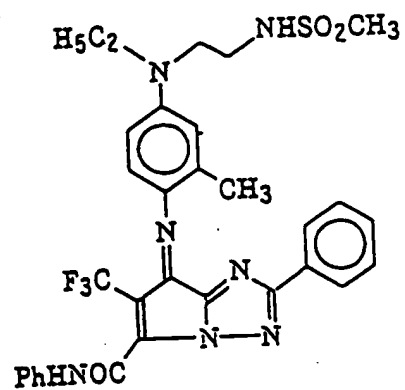
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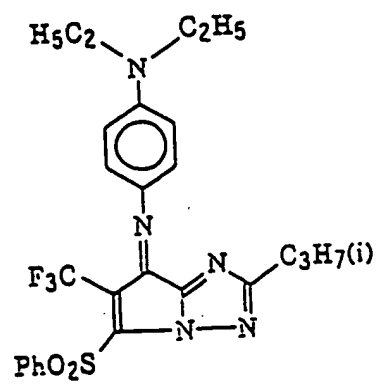
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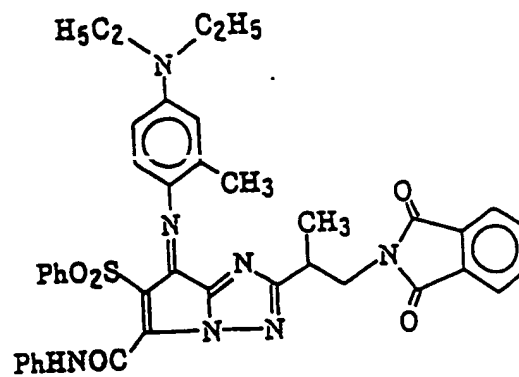
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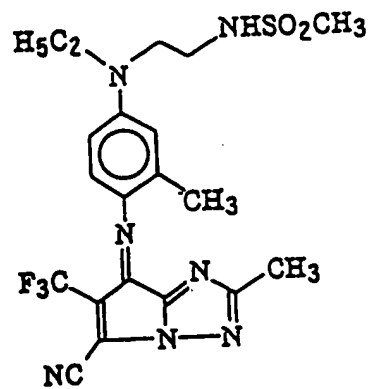
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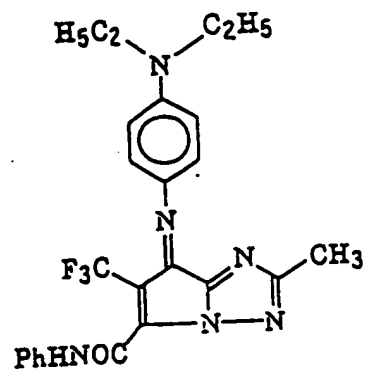
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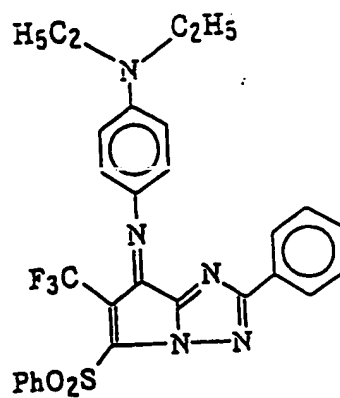
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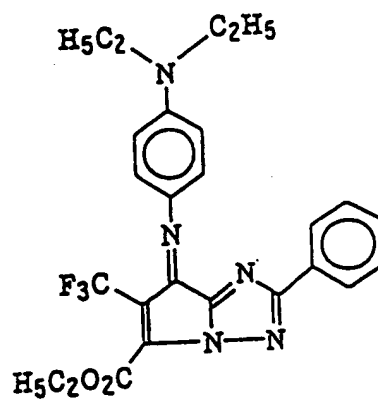
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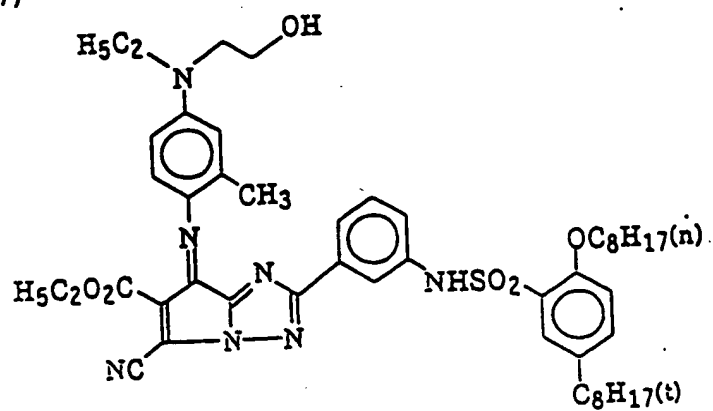
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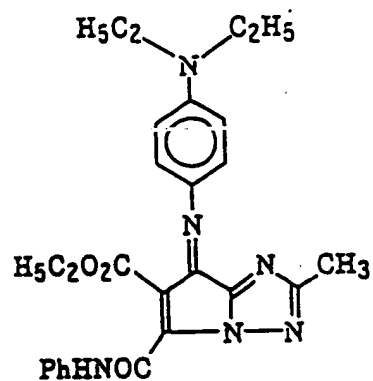
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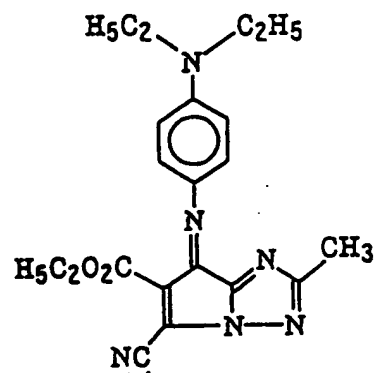
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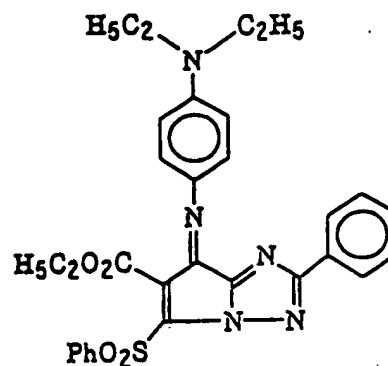
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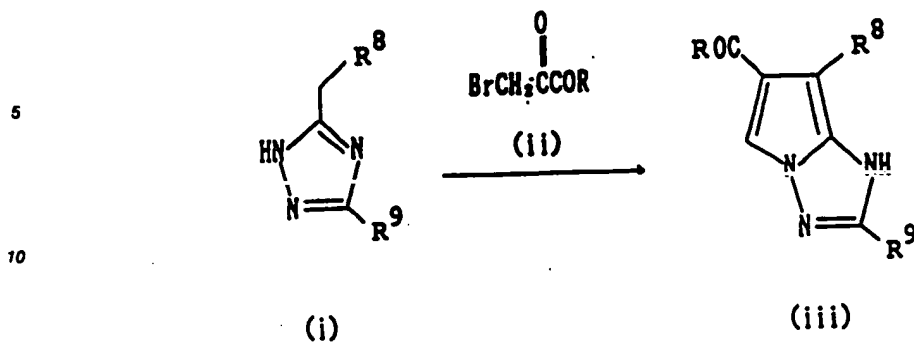
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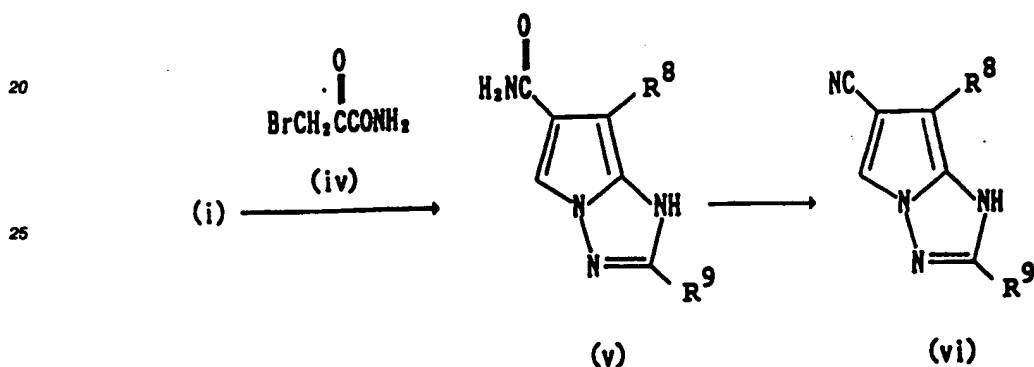
(II-30)



Typical examples of process for the synthesis of the compound represented by formula (III) will be given below. When R<sup>7</sup> = COR:



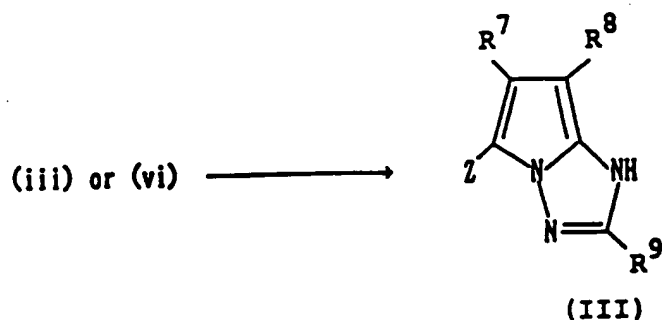
15 When  $R^7 = \text{CN}$ :



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50 Compound (i) can be synthesized by any known method. For example, synthesis methods as described in J. C. S., 518 (1961), J. C. S., 5149 (1962), *Angew. Chem.*, 72,956 (1960), and *Berichte.*, 97,3436 (1964), and references cited therein, and analogous methods can be used.

The synthesis of Compound (iii) can be accomplished by the nucleophilic displacement reaction from Compound (i) to Compound (ii) and the subsequent cyclization reaction.

55 In this synthesis, a base such as sodium hydride, triethylamine, diazabicycloundecene, potassium carbonate and sodium carbonate may be preferably used. The reaction may be effected free of solvent or in a solvent such as tetrahydrofuran, acetonitrile, N,N-dimethylformamide, N,N-dimethylacetamide, N,N'-dimethylimidazolidon-2-one, acetone and toluene. The reaction temperature is normally in the range of

-20°C to 150°C, preferably 0°C to 100°C.

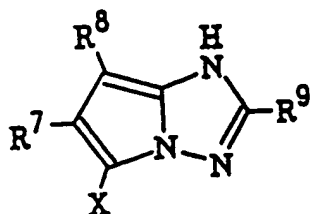
The synthesis of Compound (v) can be accomplished by the nucleophilic displacement reaction from Compound (i) to Compound (iv) and the subsequent cyclization reaction as in the synthesis of Compound (iii).

- 5 Compound (vi) is derived by the dehydration reaction of Compound (v). In this reaction, phosphorus oxychloride, phosphorus pentachloride, phosphorus trichloride, etc. may preferably be used. The reaction may be effected free of solvent or in toluene or chloroform. The reaction temperature is normally in the range of -10°C to 250°C, preferably 20°C to 200°C.

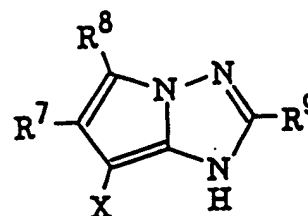
- 10 The compound represented by formula (III) can be synthesized from Compound (iii) or (vi) by a known method.

- For example, if an arylthio group or heterocyclic thio group is connected to Compound (III) to obtain a 7-aromatic mercapto or heterocyclic mercapto substituted compound, a method described in U.S. Patent 3,227,554 can be used, i.e., a process can be used which comprises dissolving an aryl-mercaptan, heterocyclic mercaptan and their disulfides in a halogenated hydrocarbon solvent, treating the solution with chlorine or sulfonyl chloride to produce sulfonyl chloride, and then adding the solution to a solution of Compound (III) in an aprotic polar solvent.

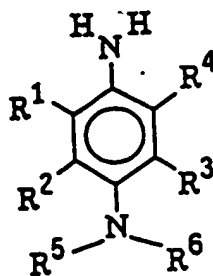
The compounds represented by formulae (I) and (II) can be synthesized by oxidation coupling of the following Compound A or B with the following Compound C:



30 (A)



(B)

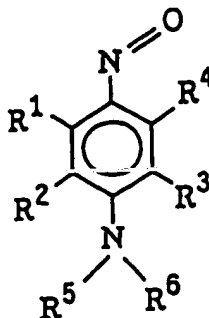


(C)

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In these formulae, X represents a hydrogen atom or split-off group which splits off upon coupling reaction, and formula (A) includes formula (III). It goes without saying that Compounds A and B may be in the form of their tautomers.

- 55 Alternatively, the compounds represented by formulae (I) and (II) can be synthesized by the dehydration condensation of the above mentioned Compound A or B with the following Compound D:



(D)

20 In this case, X in Compounds A and B is a hydrogen atom.

For example, the compound represented by formula (I) can be derived from the compound represented by formula (III) by a known method as described in JP-A-63-145281. That is, the compound represented by formula (I) can be synthesized in the presence of a compound represented by formula (III), a phenylenediamine, and an oxidizer.

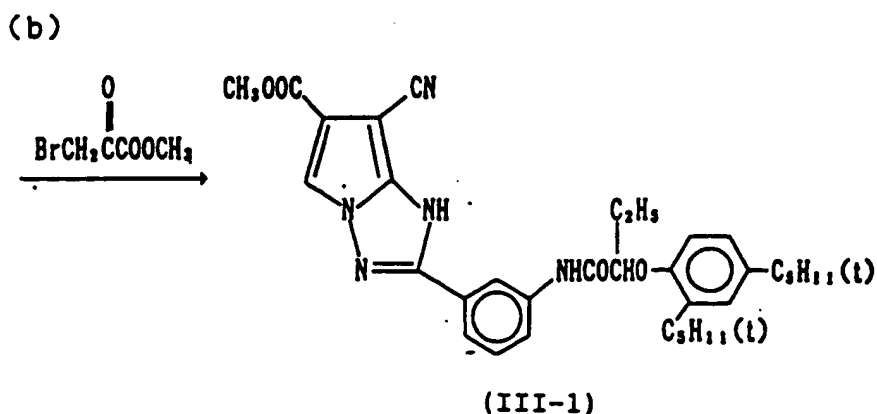
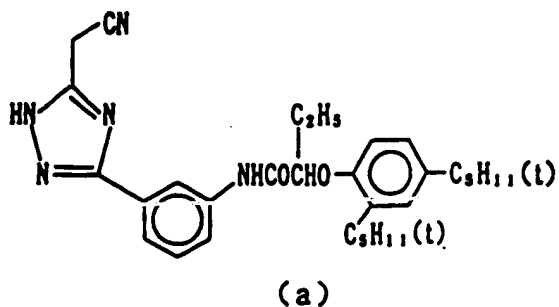
25 It is thought that this coupling reaction involves a nucleophilic attack of a coupler anion on quinodimine produced by the oxidation of phenylenediamine to form a leuco dye which is then converted to an azomethine dye as described in T. H. James, *The Theory of the Photographic Process*, 4th ed., Macmillan, 1977. The reaction preferably proceeds under a basic condition. The reaction medium may be any of an organic medium, aqueous organic medium and aqueous solution. If the reaction is effected in a basic aqueous solution, the compound represented by formula (III) may be an oil-in-water dispersion. The oil-in-water dispersion may be present in a hydrophilic colloidal medium such as gelatin. As the oxidizer there may be used any organic or inorganic oxidizer having a potential strong enough to oxidize phenylenediamine. The oxidizer may be used in the form of solution or dispersion in the reaction medium. If Z in formula (III) is a hydrogen atom, phenylenediamine is present in the system in an amount of 0.1 to 10 mol, preferably 0.5 to 2 mol per mol of compound of formula (III), and the oxidizer is used in an amount of at least 4 equivalents, preferably 4.4 to 20 equivalents. If Z is not a hydrogen atom, the compound represented by formula (I) can be synthesized in the same manner as above except that the oxidizer is used in an amount of at least 2 equivalents, preferably 2.2 to 10 equivalents. If the reaction medium is aqueous, coupling may be effected at a pH of 8 or more, preferably 10 to 12. As the oxidizer there can be used silver halide, hydrogen peroxide, manganese dioxide, potassium persulfate, oxygen, or compounds as described in Fieser & Fieser, *Organic Reagents*.

The present invention will be further described in the following examples, but the present invention should not be construed as being limited thereto.

#### 45 EXAMPLE 1: Synthesis of Compound (III-1)

Compound (III-1) was synthesized in the following process:

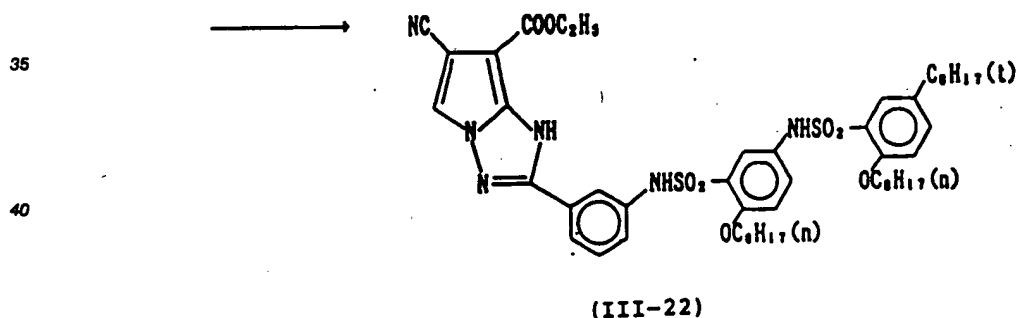
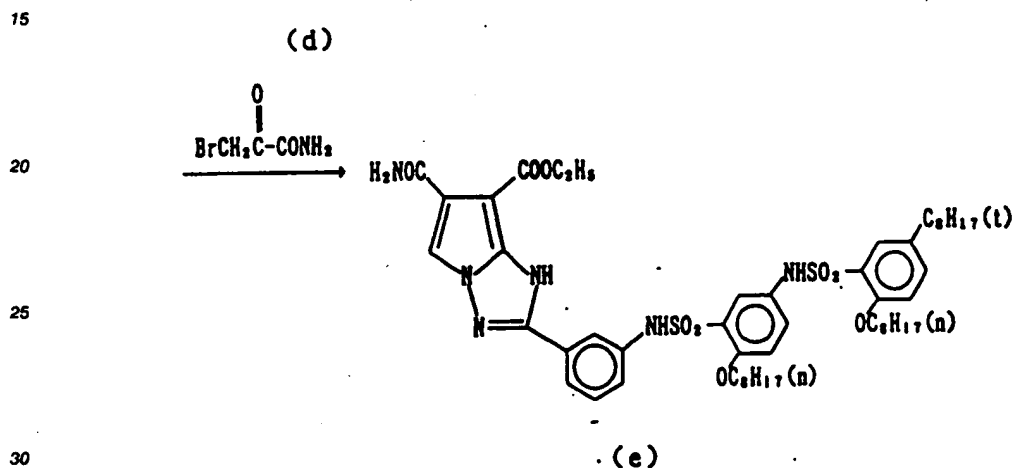
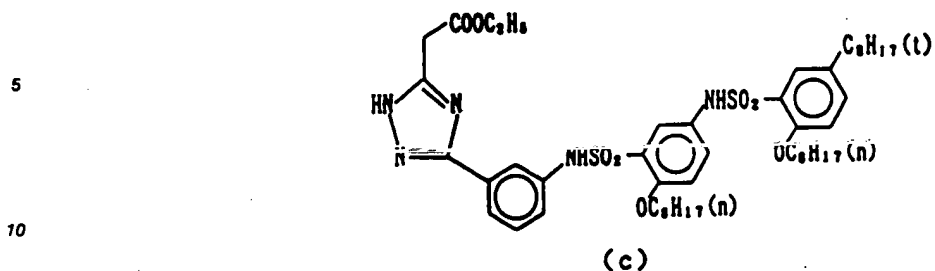




To a solution of Compound (a) (50.1 g; 0.1 mol) and Compound (b) (19.9 g; 0.11 mol) in tetrahydrofuran (300 ml) was added gradually sodium hydride (12.0 g; 0.30 mol) at a temperature of 0 °C in such a manner that the reaction temperature didn't rise. The reaction system was stirred for 1 hour. 200 ml of a 1 N dilute hydrochloric acid was added to the reaction system. The reaction system was extracted with 300 ml of ethyl acetate three times. The resulting organic phase was washed with water and saturated brine, and then dried over anhydrous sodium sulfate. The solvent was distilled off under reduced pressure. The material was purified through column chromatography (developing solvent: 3 : 1 mixture of hexane and ethyl acetate) to obtain 7.57 g of Compound (III-1) (yield: 13%).

#### EXAMPLE 2: Synthesis of Compound (III-22)

Compound (III-22) was synthesized in the following process:



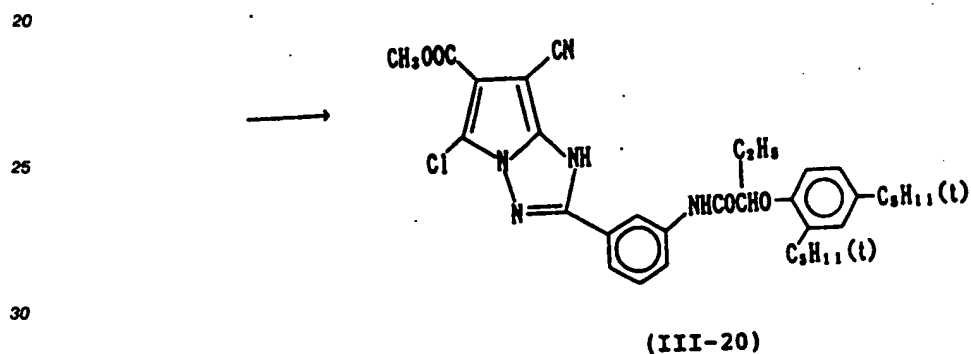
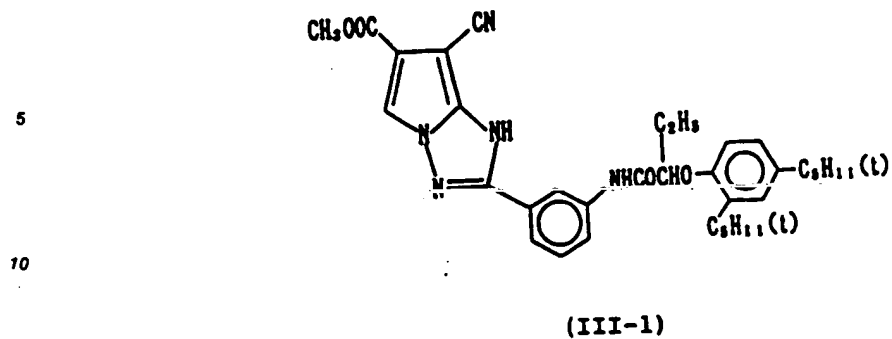
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From Compound (c) (45.5 g; 50 mmol) and Compound (d) (9.13 g; 55 mmol) Compound (e) was obtained in the same manner as in Synthesis Example 1 (3.90 g; 8%). To Compound (e) (3.90 g; 4.0 mmol) was added phosphorus oxychloride (1.47 g; 9.6 mmol) at a temperature of 100 °C. The reaction system was stirred for 1 hour. After the reaction system was cooled, 10 cc of water was added thereto. The reaction system was extracted with 30 cc of ethyl acetate three times. The resulting organic phase was washed with saturated brine, and then dried over anhydrous sodium sulfate. The solvent was distilled off under reduced pressure. The material was recrystallized from acetonitrile (30 cc) to obtain 3.22 g of Compound (III-22) (yield: 84%).

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**EXAMPLE 3: Synthesis of Compound (III-20)**

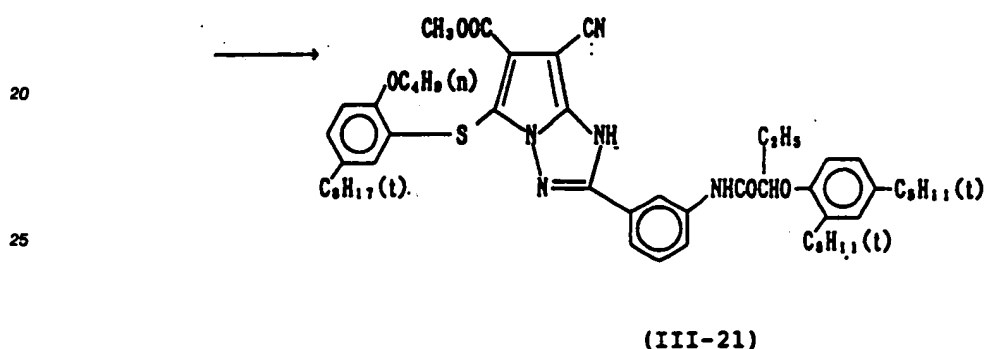
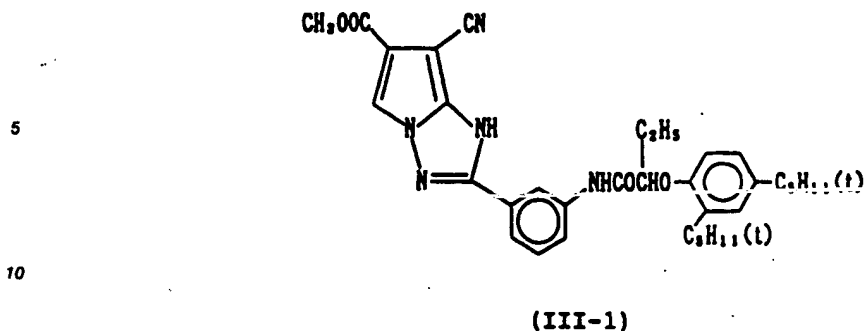
Compound (III-20) was synthesized in the following process:



35 To a solution of Compound (III-1) (2.91 g; 5 mmol) in methylene chloride (30 ml) was added dropwise  
 40 sulfuryl chloride (0.74 g; 5.5 mmol) at a temperature of 0°C. The reaction system was stirred for 1 hour.  
 Water was added to the reaction system. The reaction system was extracted with 30 cc of methylene  
 chloride three times. The resulting organic phase was washed once with saturated brine, and then dried  
 over anhydrous sodium sulfate. The solvent was distilled off under reduced pressure. The material was  
 recrystallized from acetonitrile to obtain 2.83 g of Compound (III-20) (yield: 92%).

#### EXAMPLE 4: Synthesis of Compound (III-21)

Compound (III-21) was synthesized in the following process:



30

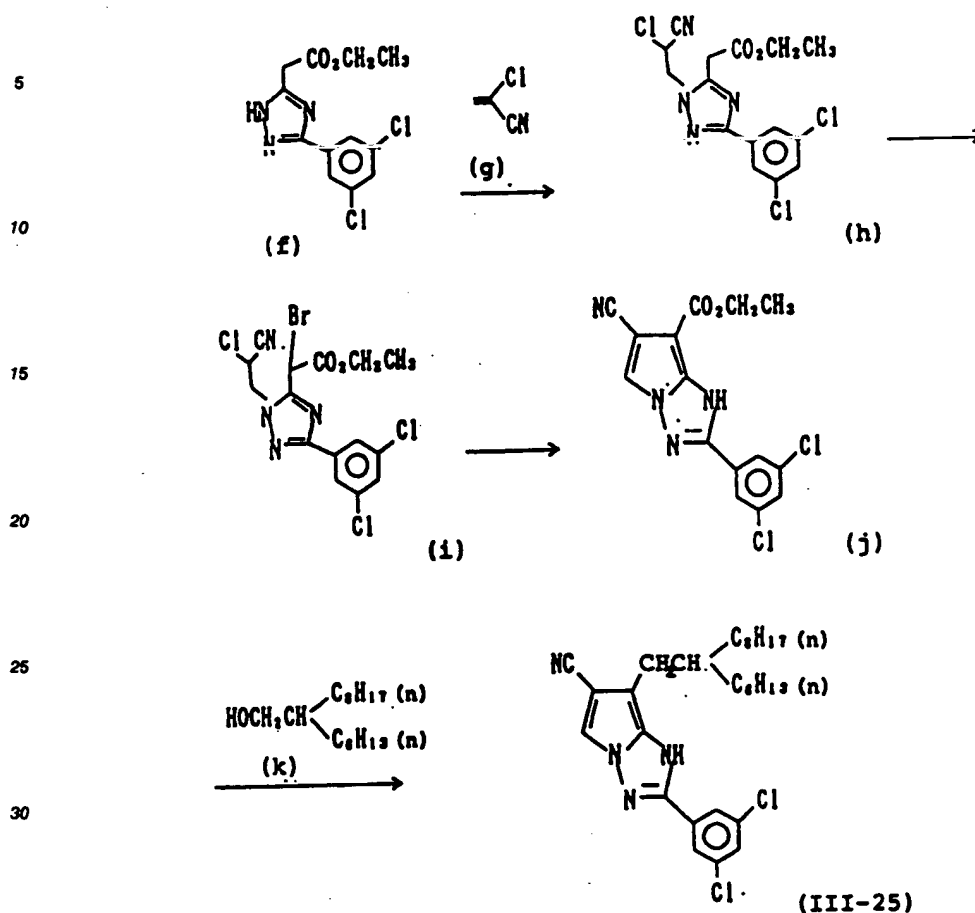
To a solution of di-[(2-n-butoxy-5-t-octyl)phenyl]disulfide (3.53 g; 6 mmol) in methylene chloride (20 ml) was added sulfuryl chloride (1.78 g; 13 mmol) at a temperature of 0 °C. The reaction system was stirred for 1 hour. Methylene chloride and sulfuryl chloride were removed under reduced pressure. To the residue was added methylene chloride (20 ml). The solution was added dropwise to a solution of Compound (III-1) (2.91 g; 5 mmol) in N,N-dimethylformamide (10 ml) at a temperature of 0 °C. The reaction system was stirred for 1 hour. Water was added to the reaction system. The reaction system was extracted with 30 ml of ethyl acetate twice. The resulting organic phase was washed with water and saturated brine, and then dried over anhydrous sodium sulfate. The solvent was distilled off under reduced pressure. The material was purified through silica gel chromatography (developing solvent: 2 : 1 mixture of hexane and ethyl acetate) to obtain 2.93 g of Compound (III-21) (yield: 67%).

#### EXAMPLE 5: Synthesis of Compound (III-25)

45 Compound (III-25) was synthesized in the following process:

50

55



30.0 g of Compound (f) and 11.4 g of Compound (g) were dissolved in 300 ml of tetrahydrofuran. 6.0 ml of tetramethyl guanidine was added to the solution. The material was stirred at room temperature for 5 hours. 500 ml of ethyl acetate was added to the material. The material was then washed with water. The ethyl acetate was dried, and then distilled off. The material was then crystallized from methanol to obtain 27.5 g of Compound (h).

27.4 g of Compound (h) thus obtained was dissolved in 270 ml of tetrahydrofuran. 13.6 g of bromine was gradually dropwise added to the solution under cooling with ice. The material was stirred for 5 hours. 500 ml of ethyl acetate was added to the material. The material was then washed with water until it turned neutral. The resulting ethyl acetate phase was dried, and then distilled off. The residue was purified through column chromatography to obtain 28.0 g of Compound (i).

28.0 g of Compound (i) thus obtained was dissolved in 170 ml of tetrahydrofuran. 9.6 g of 60% sodium hydride was gradually added to the material while the reaction temperature was kept at  $-10^{\circ}\text{C}$ . After the completion of the reaction, ethyl acetate was added to the reaction system. The material was then washed with water. The resulting ethyl acetate phase was dried, and then distilled off. The material was purified through column chromatography to obtain 3.0 g of Compound (j).

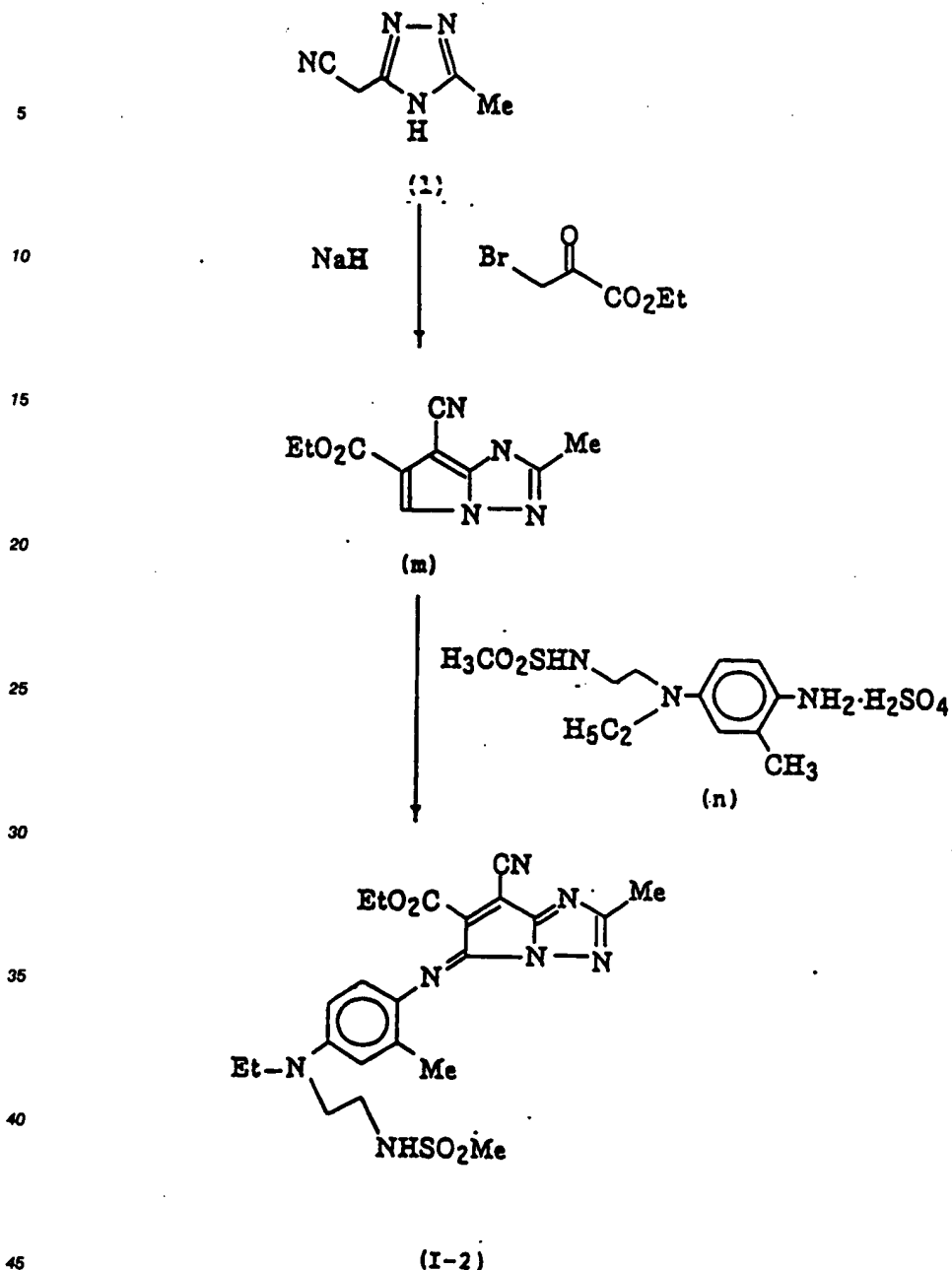
1.8 g of Compound (j) thus obtained and 12.4 g of Compound (k) were dissolved in 2.0 ml of sulfolane. To the solution was further added 1.5 g of titanium isopropoxide. The reaction system was then allowed to undergo reaction for 1.5 hours while the reaction temperature was kept at  $110^{\circ}\text{C}$ . Ethyl acetate was then added to the material. The material was then washed with water. The resulting ethyl acetate phase was dried, and then distilled off. The residue was then purified through column chromatography to obtain 1.6 g of Compound (III-25).

The melting point of Compound (III-25) was  $97$  to  $98^{\circ}\text{C}$ .

**EXAMPLE 6: Synthesis of Dye of Compound (III-20)**

To a solution of Compound (III-20) (9.59 g; 10.0 mmol) in 100 ml of a 1 : 1 mixture of ethyl acetate and ethanol was added 40 ml of an aqueous solution of sodium carbonate (9 g). Subsequently, 4-(N-ethyl-N-(2-methanesulfonamidoethyl)amino)-2-methylaniline sulfate (6.38 g; 12.2 mmol) was added to the system. The material was then stirred at room temperature for 5 hours. To the material was then added dropwise 20 ml of an aqueous solution of ammonium persulfate (4.5 g). The material was then stirred for 1 hour. The material was then extracted with ethyl acetate three times. The resulting organic phase was washed with saturated aqueous solution of sodium chloride, and then dried over anhydrous sodium sulfate. The solvent was then distilled off under reduced pressure. The material was then purified through column chromatography (developing solvent: 20 : 1 mixture of methylene chloride and methanol). The material was then recrystallized from methanol to obtain 10.2 g of a dye of Compound (III-20) (yield: 83%).

**EXAMPLE 7: Synthesis of Compound (I-2)**



1.5 g of 3-cyanomethyl-5-methyl-1,2,4-triazole (Compound (1)) was dissolved in 30 ml of tetrahydrofuran. To the solution was added 1.0 g (24.8 mmol) of sodium hydride (60% in oil). The material was then heated to a temperature of 50°C. To the material was added 1.9 ml (14.7 mmol) of ethyl bromopyruvate. The material was further heated under reflux for 2 hours. The material was then cooled to room temperature. To the material were then added brine and 2 N hydrochloric acid solution to acidify the solution. The material was extracted with ethyl acetate twice, and then dried. Ethyl acetate was then distilled off under reduced pressure. The residue was then purified through silica gel chromatography to obtain 1.20 g of Compound (m) (yield: 45%).

The synthesis of Compound (1) was accomplished by a method described in Journal of the Chemical Society, 5149 (1962).

To 1.0 g of Compound (m), 20 cc of ethyl acetate, 20 cc of ethanol, 24 cc of water, 6.6 g of sodium carbonate and 3.1 g of Compound (n) was added a solution of 4.6 g of ammonium persulfate in 5 cc of water with stirring.

The reaction system was then allowed to undergo reaction at a temperature of 20°C for 1 hour. The material was then extracted with ethyl acetate. The resulting organic phase was washed with water twice, and then dried over magnesium sulfate. After filtration, the solvent was distilled off. The resulting crude crystal was purified through silica gel chromatography, and then recrystallized from methanol to obtain 0.82 g of Compound (l-2) (yield: 37%; m.p. 223 to 224°C)

The absorption characteristics of Compound (l-2) of the present invention in a solvent are shown in Fig. 1 together with those of Comparative Dye a.

In Fig. 1, the solid line indicates the absorption characteristics of Compound (l-2) of the present invention, and the broken line indicates the absorption characteristics of Comparative Dye a.

The maximum absorption wavelength ( $\lambda_{max}$ ) and half-value width of Compound (l-2) of the present invention and Comparative Dye a are set forth below.

#### Compound (l-2) of the present invention

$\lambda_{max}$ : 602.3 nm (in ethyl acetate)

Half-value width: 94.9 nm

#### Comparative Dye

$\lambda_{max}$ : 582.6 nm (in ethyl acetate)

Half-value width: 88.1 nm

As the comparative dye there was used Comparative Dye a shown below:

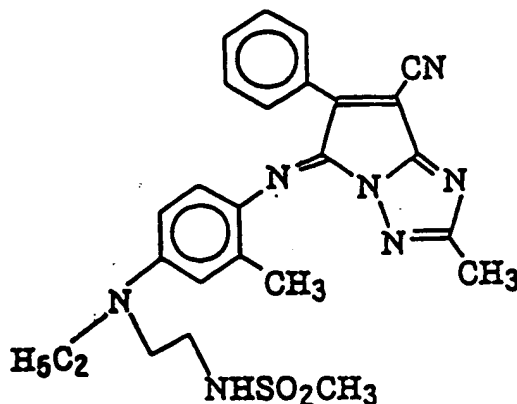


Fig. 1 shows that the dye of the present invention exhibits a sharp absorption, a reduced undesirable absorption in the yellow portion and a maximum absorption suitable as cyan dye.

On the other hand, it is shown that Comparative Dye a wherein the substituent  $R^7$  in the coupler portion is a phenyl group ( $\sigma_p$  is smaller than 0.15) doesn't exhibit cyan color.

The maximum absorption wavelength ( $\lambda_{max}$ ) of other exemplary compounds of the present invention in ethyl acetate are set forth below:

|                  |        |
|------------------|--------|
| Compound (l-22): | 618 nm |
| Compound (l-4):  | 606 nm |
| Compound (l-7):  | 619 nm |
| Compound (l-10): | 616 nm |



REFERENTIAL EXAMPLE 1

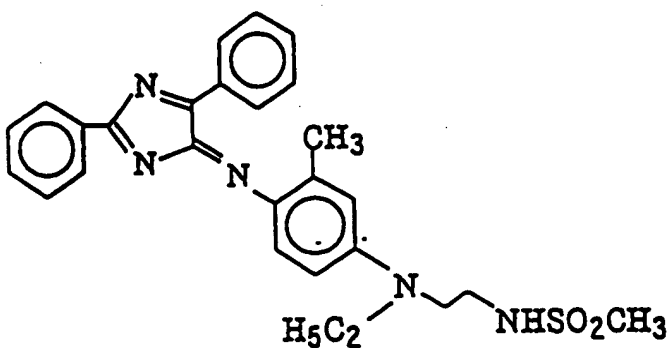
The dyes of the present invention were examined for fastness to light in a solution system. The dyes thus examined and the test results are set forth in Table 1.

|    |                  |   |
|----|------------------|---|
| 5  | Condition:       | merry-go-round type xenon radiator (produced by Dojun Koki K.K.; output: 500 W, 100,000 lux)                          |
|    | Cell:            | quartz cell   |
|    | Solvent:         | acetonitrile  |
|    | Concentration:   | $3.0 \times 10^{-5}$ (mol/l)  |
| 10 | Percent residue: | represented by the change (%) in the concentration at $\lambda_{\max}$ from before to after forced discoloration test |

Table 1

|    |            |                               |                                     |                            |                |
|----|------------|-------------------------------|-------------------------------------|----------------------------|----------------|
| 15 | <u>Dye</u> | <u>Irradia-<br/>tion Time</u> | <u>Ultraviolet<br/>Light Filter</u> | <u>Percent<br/>Residue</u> | <u>Remarks</u> |
|    | I-2        | 60 min.                       | None                                | 50                         | Invention      |
| 20 | I-4        | "                             | "                                   | 59                         | "              |
|    | I-7        | "                             | "                                   | 54                         | "              |
|    | I-10       | "                             | "                                   | 62                         | "              |
| 25 | b          | "                             | "                                   | 43                         | Comparison     |

30 Comparative Dye b:

REFERENTIAL EXAMPLE 2

50 In order to demonstrate the usefulness of the dyes of the present invention as filter dyes, the following model filters were prepared and examined for fastness to light.

Onto a 100- $\mu$ m thick polyethylene terephthalate film (produced by Teijin Limited) which had been rendered heat resistant and smoothened on its back side as a support was coated a dye dispersion layer  
55 coating composition having the following formulations by a wire bar coating process to prepare a model filter. The thickness of the coating was adjusted such that the density after drying reached 2.0.

Dye dispersion layer coating composition:

|  |        |
|--|--------|
| Dye (I-1)  | 1.0 g  |
| Polyvinyl butyral resin (Denka Butyral 5000-A produced by Denki Kagaku Kogyo K.K.) | 3.0 g  |
| Toluene  | 50 cc  |
| Methyl ethyl ketone  | 50 cc  |
| Polyisocyanate (Takenate D110N produced by Takeda Chemical Industries, Ltd.)       | 0.2 cc |

Model filters were prepared in the same manner as above except that Dye (I-1) was replaced by other dyes set forth in Table 2.

The model filters thus prepared were irradiated with light from a 17,000 lux fluorescent lamp for 14 days to examine the stability of the dyes. For evaluation of the dye stability, the ratio of the density measured before to after irradiation was determined. The results are set forth in Table 2.

**Table 2**

| <u>Dye</u> | <u>Percent Residue</u> | <u>Remarks</u> |
|------------|------------------------|----------------|
| I-1        | 95                     | Invention      |
| I-2        | 93                     | "              |
| I-4        | 94                     | "              |
| I-7        | 94                     | "              |
| I-10       | 95                     | "              |
| b          | 85                     | Comparison     |

The results set forth above show that the dyes of the present invention exhibit a remarkable fastness to light as compared with the comparative dyes.

### REFERENTIAL EXAMPLE 3

Onto a commercially available uncoated base paper (basis weight: 64 g/m<sup>2</sup>) was coated a coating solution consisting of 43 parts (by weight calculated in terms of solid content, hereinafter the same) of finely divided hollow grains of a styrene-acrylic ester copolymer (grain diameter: 0.3 to 0.4  $\mu$ m), 17 parts of vapor phase process anhydrous silica (grain diameter: 12 nm), 12 parts of a styrene-butadiene copolymer latex, 18 parts of a polyvinyl acetate latex and 10 parts of finely divided grains of polymethyl methacrylate (grain diameter: about 8  $\mu$ m) by means of a wire bar in such an amount that the solids content reached 10 g/m<sup>2</sup> to prepare a paper for ink jet recording.

Ink jet recording was made on this recording paper with Ink A having the following formulations. In this ink jet recording, an electrostatic acceleration type ink jet apparatus equipped with a head having a nozzle pore diameter of 50  $\mu$ m and a dot density of 8/mm was used.

#### Ink A:

|                                    |      |
|------------------------------------|------|
| Dye (I-1) of the present invention | 6 g  |
| Diethyl phthalate                  | 30 g |
| Diisopropyl adipate                | 44 g |
| N,N-Diethyldodecanamide            | 20 g |

This ink exhibited an excellent dischargeability, and a sharp and high density cyan image was obtained.

Similar ink jet recording tests were effected except that Dye (I-1) was replaced by Dyes (I-7) and (I-10), respectively, in the same gram equivalent. As a result, all these dyes exhibited an excellent ink dischargeability and thus provided sharp and high density cyan images.

After these images were allowed to stand under indoor light for 3 months, the density thereof showed a drop of 1% or less.

#### REFERENTIAL EXAMPLE 4

(Preparation of heat transfer material)

The following materials were sufficiently dispersed in admixture to prepare a coating solution for smooth heat-resistant protective layer.

Formulations of coating solution:

|                         |       |
|-------------------------|-------|
| Methyl methacrylate     | 10 g  |
| n-Butyl acrylate        | 2 g   |
| Benzoyl peroxide        | 0.1 g |
| Silica                  | 35 g  |
| Isopropyl alcohol (IPA) | 15 g  |

The coating solution was diluted with a proper amount of a mixture of toluene and IPA. The coating solution was then coated on a 6- $\mu$ m thick polyethylene terephthalate film (hereinafter referred to as "PET") as a substrate by means of a wire bar. The coated material was then dried at a temperature of 100°C for 1 minute to form a smooth heat-resistant protective layer with a thickness of about 1.5  $\mu$ m.

A hot-melt ink having the following formulations was prepared.

Formulations of hot-melt ink:

|                                   |       |
|-----------------------------------|-------|
| Dye (I-1)                         | 10 g  |
| Barium salt of lanolin fatty acid | 30 g  |
| Carnauba wax                      | 20 g  |
| Paraffin wax                      | 20 g  |
| Dispersant                        | 0.5 g |
| Liquid paraffin                   | 5 g   |

The ink having the above mentioned formulations was then sufficiently dispersed with a mixture of 100 cc of methyl ethyl ketone and 130 cc of toluene at a temperature of 68°C by a ball mill for about 48 hours.

To the ink dispersion was added 300 g of a 20 wt.% vinyl chloride-vinyl acetate copolymer resin solution (10 parts of resin, 20 parts of toluene, 20 parts of methyl ethyl ketone). The mixture was then dispersed by a ball mill for about 1 hour to prepare a coating solution of heat-sensitive transfer composition.

This coating solution was coated on the surface of the above mentioned PET film opposite the smooth heat-resistant protective layer by means of a wire bar, and then dried at a temperature of 100°C for 1 minute to form a hot-melt ink layer having a thickness of about 5  $\mu$ m.

The heat transfer material thus obtained was laminated with a plain paper as a heat transfer image-receiving material in such an arrangement that the transfer layer (hot-melt ink layer) in the heat transfer material was brought into contact with the plain paper. Printing was effected by a heat head on the heat transfer material from the support side to cause transfer. As a result, a sharp cyan color recording was provided.

Heat transfer materials were prepared in the same manner as above except that Dye (I-1) was replaced by Dyes (I-7) and (I-10), respectively, in the same gram equivalent weight. Using these heat transfer materials, transfer was similarly effected. As a result, a sharp cyan color recording was provided.

These recorded sheets were then examined for stability of image to light. A high image stability to light was obtained.

The derivatives represented by formula (III) of the present invention are useful as synthesis intermediates of physiologically active substances such as pharmaceutical preparations and pesticides. These derivatives are also useful as couplers in the field of photographic chemistry.

On the other hand, the compounds represented by formulae (I) and (II) are useful dyes which are advantageous in that they exhibit a reduced secondary absorption and a primary absorption wavelength of 600 nm or more.

When used as an image forming dye in ink jet recording process, heat-sensitive transfer recording process, etc., the novel pyrrolotriazole azomethine dye of the present invention provides a high density image free of discoloration because of its remarkably excellent fastness to light.

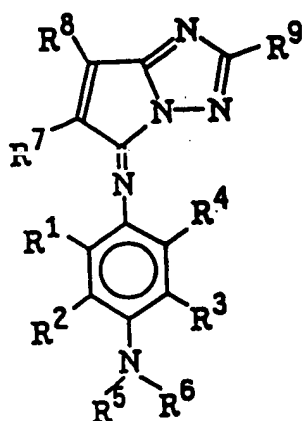
Also, when used as various filter dyes, the azomethine dye of the present invention provides a filter with an excellent stability and a remarkably reduced density drop because of its excellent fastness to light.

Furthermore, when image formation is effected on a heat transfer dye providing material comprising the pyrrolotriazole azomethine dye of the present invention, it provides an image with a high fastness to heat and light and an excellent color reproducibility.

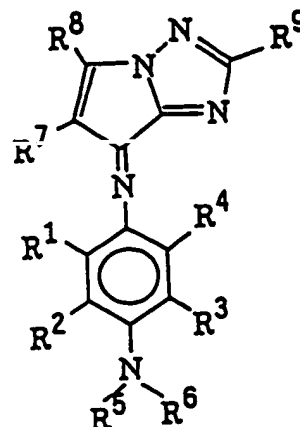
Moreover, the pyrrolotriazole azomethine dye of the present invention provides the heat transfer dye providing material with a better storage stability when used in admixture with one or more present azomethine dyes than when used singly.

#### Claims

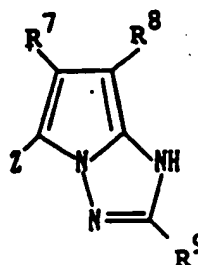
1. A pyrrolotriazole derivative represented by any one of formulae (I), (II), or (III):



(I)



(II)



(III)

wherein:

$R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  each independently represents a hydrogen atom or a nonmetallic atomic group;

$R^5$  and  $R^6$  each independently represents a hydrogen atom, alkyl group, an aryl group, or a heterocyclic group;

$R^7$  represents an electrophilic group having a Hammett's substituent constant  $\sigma_p$  of 0.15 or more;

$R^8$  and  $R^9$  each independently represents a hydrogen atom or a nonmetallic atomic group;

the sum of Hammett's substituent constant  $\sigma_p$  of  $R^7$  and  $R^8$  is 0.65 or more;

$R^1$  and  $R^2$ , and/or  $R^2$  and  $R^5$ , and/or  $R^5$  and  $R^6$ , and/or  $R^6$  and  $R^3$ , and/or  $R^3$  and  $R^4$  may be connected to each other to form a cyclic structure;

$R^7$  and  $R^8$  may be connected to each other to form a cyclic structure; and

Z represents a hydrogen atom, a halogen atom, an arylthio group, a heterocyclic thio group, an arylsulfinyl group, or a nitroso group.

2. A pyrrolotriazole derivative as in claim 1, wherein said pyrrolotriazole derivative is a pyrrolotriazole azomethine dye represented by any one of formulae (I) or (II).

3. A pyrrolotriazole derivative as in claim 1, wherein said pyrrolotriazole derivative is a 1H-pyrrolo-[1,2-b]-[1,2,4]triazole derivative represented by formula (III).

4. A pyrrolotriazole derivative as in claim 1, wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> each independently represents a hydrogen atom, a halogen atom, an alkyl group, an aryl group, a heterocyclic group, a cyano group, a hydroxyl group, a nitro group, a carboxyl group, a sulfonic acid group, an amino group, an alkoxy group, an aryloxy group, an acylamino group, an aminocarbonylamino group, a sulfamoylamino group,  
 5 an alkylthio group, an arylthio group, an alkoxycarbonylamino group, a sulfonylamino group, a carbamoyl group, a sulfamoyl group, a sulfonyl group, an alkoxycarbonyloxy group, a heterocyclic oxy group, an azo group, an acyloxy group, a carbamoyloxy group, a silyloxy group, an aryloxy carbonyl group, an imido group, a heterocyclic thio group, a sulfinyl group, a phosphoryl group, a formyl group, an acyl group, or an azolyl group.
- 10 5. A pyrrolotriazole derivative as in claim 4, wherein R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> each represents a hydrogen atom; and R<sup>1</sup> represents a hydrogen atom, an alkyl group, or an acylamino group.
6. A pyrrolotriazole derivative as in claim 1, wherein said electrophilic group having a Hammett's  
 15 substituent constant  $\sigma_p$  of 0.15 or more for R<sup>7</sup> is a formyl group, an acyl group, an acyloxy group, a carbamoyl group, an alkoxycarbonyl group, an aryloxy carbonyl group, a cyano group, a carboxyl group, a nitro group, a dialkylphosphono group, a diarylphosphono group, a diarylphosphinyl group, an alkylsulfinyl group, an arylsulfinyl group, an alkylsulfonyl group, an arylsulfonyl group, an arylthio group, a sulfonyloxy group, an acylthio group, a sulfamoyl group, an isocyanato group, a thiocyanato group, a  
 20 thiocarbonyl group, an alkyl group substituted by at least two halogen atoms, an alkoxy group substituted by at least two halogen atoms, an aryloxy group substituted by at least two halogen atoms, an alkylamino group substituted by at least two halogen atoms, an alkylthio group substituted by at least two halogen atoms, an aryl group substituted by other electrophilic groups having a Hammett's substituent constant  $\sigma_p$  of 0.15 or more, a heterocyclic group, a chlorine atom, a bromine atom, or a  
 25 selenocyanato group.
7. A pyrrolotriazole derivative as in claim 6, wherein said electrophilic group having a Hammett's substituent constant  $\sigma_p$  of 0.15 or more for R<sup>7</sup> is a cyano group or a -COR group, wherein R represents a hydrogen atom, an amino group, an alkoxy group, or an aryloxy group.
- 30 8. A pyrrolotriazole derivative as in claim 1, wherein R<sup>8</sup> represents a hydrogen atom, an aryl group, a heterocyclic group, an alkyl group, a cyano group, a carboxyl group, a formyl group, an acyl group, a carbamoyl group, an alkoxycarbonyl group, an aryloxy carbonyl group, an acylamino group, an alkoxycarbonylamino group, an aryloxy carbonylamino group, a sulfonylamino group, an aminocarbonylamino group, a sulfamoylamino group, an amino group, an alkoxy group, an aryloxy group, a silyloxy group, a  
 35 heteroxy group, an alkylthio group, an arylthio group, a heterylthio group, a halogen atom, a hydroxyl group, a nitro group, a sulfamoyl group, a sulfonyl group, an azo group, an acyloxy group, a carbamoyloxy group, an imido group, a sulfinyl group, a phosphoryl group, or an azolyl group, provided that the sum of Hammett's substituent constant  $\sigma_p$  of R<sup>7</sup> and R<sup>8</sup> is 0.65 or more.
- 40 9. A pyrrolotriazole derivative as in claim 8, wherein R<sup>8</sup> represents a cyano group or -COR, wherein R represents a hydrogen atom, an amino group, an alkoxy group, or an aryloxy group.
10. A pyrrolotriazole derivative as in claim 1, wherein R<sup>9</sup> represents a hydrogen atom, an aryl group, a  
 45 heterocyclic group, an alkyl group, a cyano group, a carboxyl group, a formyl group, an acyl group, a carbamoyl group, an alkoxycarbonyl group, an aryloxy carbonyl group, an acylamino group, an alkoxycarbonylamino group, an aryloxy carbonylamino group, a sulfonylamino group, an aminocarbonylamino group, a sulfamoylamino group, an amino group, an alkoxy group, an aryloxy group, a silyloxy group, a  
 50 heteroxy group, an alkylthio group, an arylthio group, a heterylthio group, a halogen atom, a hydroxyl group, a nitro group, a sulfamoyl group, a sulfonyl group, an azo group, an acyloxy group, a carbamoyloxy group, an imido group, a sulfinyl group, a phosphoryl group, or an azolyl group.
11. A pyrrolotriazole derivative as in claim 10, wherein R<sup>9</sup> represents an aryl group.
- 55 12. A pyrrolotriazole derivative as in claim 11, wherein R<sup>9</sup> represents an unsubstituted aryl group or an aryl group substituted by at least one of substituents selected from a nitro group, a halogen atom, a cyano group, an acylamino group, and a sulfonamido group.

13. A pyrrolotriazole derivative as in claim 3, wherein R<sup>7</sup> and R<sup>8</sup> each independently represents a cyano group or a -COR group, wherein R represents a hydrogen atom, an amino group, an alkoxy group, or an aryloxy group; and R<sup>9</sup> represents an aryl group.

5 14. A pyrrolotriazole derivative as in claim 13, wherein Z represents a hydrogen atom; a halogen atom; an unsubstituted arylthio group; an arylthio group substituted by at least one of substituents selected from a halogen atom, an alkyl group, an alkoxy group, a cyano group, an aryloxy carbonyl group, an alkoxy carbonyl group, a ureido group, an alkoxycarbonylamino group, an acylamino group, and a carboxyl group; an unsubstituted arylsulfinyl group; or an arylsulfinyl group substituted by at least one  
10 of substituents selected from a halogen atom, an alkyl group, an alkoxy group, a cyano group, an alkoxycarbonyl group, and a carboxyl group.

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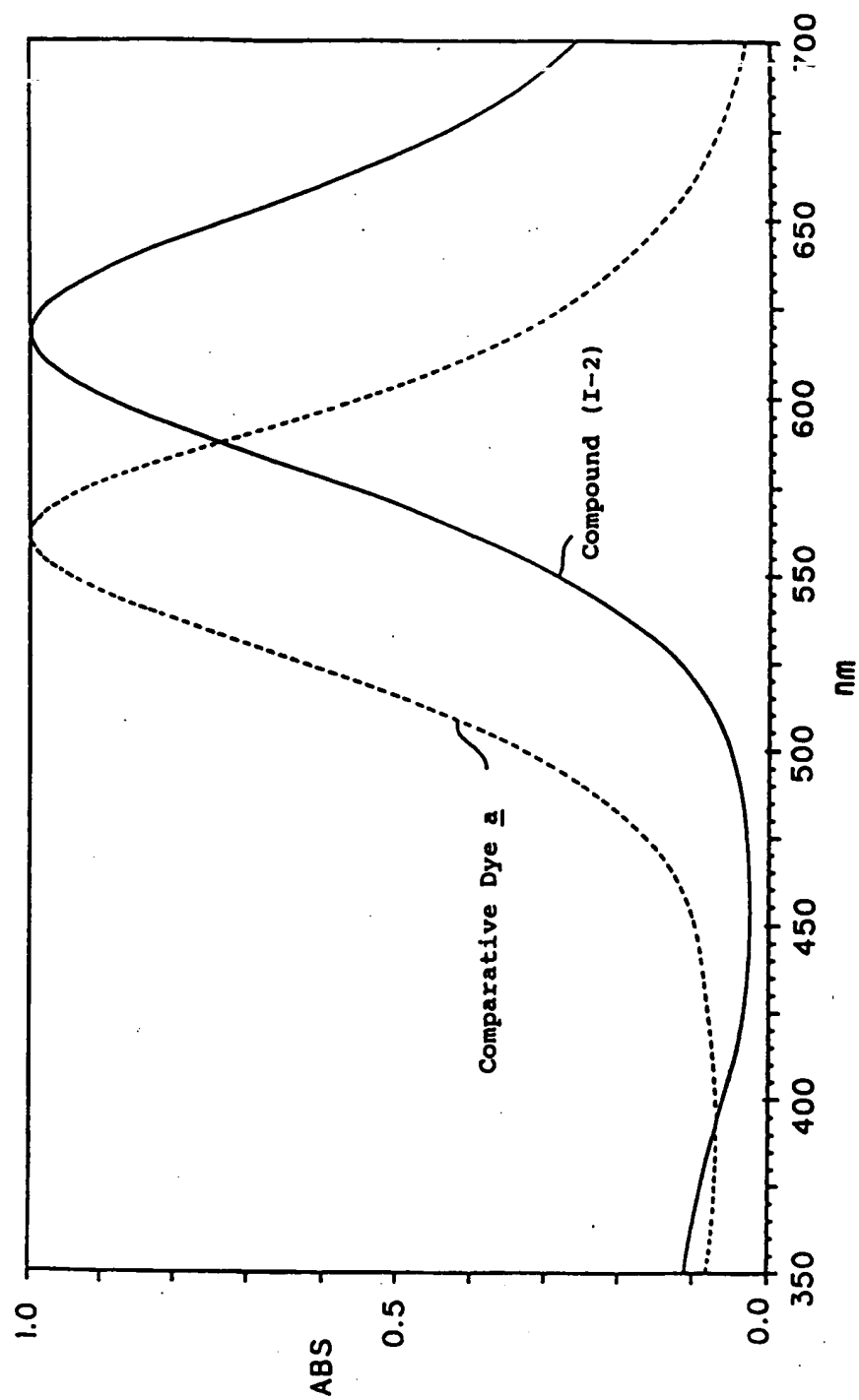
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FIG. 1







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## EUROPEAN SEARCH REPORT

Application Number

EP 92 10 9588

| DOCUMENTS CONSIDERED TO BE RELEVANT   |   |  |   |
|---|---|--|---|
| Category  | Citation of document with indication, where appropriate, of relevant passages   | Relevant to claim  | CLASSIFICATION OF THE APPLICATION (Int. Cl.5) |
| X   | EP-A-0 252 288 (KONISHIROKU SHASHIN KOGYO K.K.)<br>* page 6, line 16 - page 7, line 25; claims 1,2<br>*<br>* page 14; examples A-3 *<br>* page 16; examples C-3 *<br>* page 17, line 52 - line 55 * | 1-14   | C07D487/04                                    |
| X   | PATENT ABSTRACTS OF JAPAN<br>vol. 12, no. 180 (P-709)10 June 1986<br>& JP-A-62 289 837 (KONISHIROKU SHASHIN KOGYO K.K.) 16 December 1987  | 1,3,8-10   |   |
| A   | * abstract *  | 2,4-7,<br>11-14  |   |
| A   | US-A-4 093 728 (P.C.WADE ET AL.)<br>* column 1, line 1 - line 27; claim 1 *   | 1-14   |   |
|   |   |  | TECHNICAL FIELDS<br>SEARCHED (Int. Cl.5)      |
|   |   |  | C07D<br>B41M<br>C09B<br>G03C                  |
| The present search report has been drawn up for all claims  |   |  |   |
| Place of search<br>THE HAGUE  |   | Date of completion of the search<br>29 JULY 1992   | Examiner<br>BACON A.J.                        |
| CATEGORY OF CITED DOCUMENTS   |   |  |   |
| X : particularly relevant if taken alone<br>Y : particularly relevant if combined with another document of the same category<br>A : technological background<br>O : non-written disclosure<br>P : intermediate document |   | T : theory or principle underlying the invention<br>E : earlier patent document, but published on, or after the filing date<br>D : document cited in the application<br>L : document cited for other reasons<br>Δ : member of the same patent family, corresponding document |   |

EPO FORM 1503 (01/92) (P.4/4)



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number

EP 92 10 9588

| DOCUMENTS CONSIDERED TO BE RELEVANT   |   |  |   |
|---|---|--|---|
| Category  | Citation of document with indication, where appropriate, of relevant passages   | Relevant to claim                                | CLASSIFICATION OF THE APPLICATION (Int. Cl.5) |
| X   | EP-A-0 252 288 (KONISHIROKU SHASHIN KOGYO K.K.)<br>* page 6, line 16 - page 7, line 25; claims 1,2<br>*<br>* page 14; examples A-3 *<br>* page 16; examples C-3 *<br>* page 17, line 52 - line 55 * | 1-14   | C07D487/04                                    |
| X   | PATENT ABSTRACTS OF JAPAN<br>vol. 12, no. 180 (P-709)10 June 1986<br>& JP-A-62 289 837 ( KONISHIROKU SHASHIN KOGYO K.K. ) 16 December 1987  | 1,3,8-10   |   |
| A   | * abstract *  | 2,4-7,<br>11-14                                  |   |
| A   | US-A-4 093 728 (P.C.WADE ET AL.)<br>* column 1, line 1 - line 27; claim 1 *   | 1-14   |   |
|   |   |  | TECHNICAL FIELDS<br>SEARCHED (Int. Cl.5)      |
|   |   |  | C07D<br>B41M<br>C09B<br>G03C                  |
| The present search report has been drawn up for all claims  |   |  |   |
| Place of search<br>THE HAGUE  |   | Date of completion of the search<br>29 JULY 1992 | Examiner<br>BACON A. J.                       |
| <b>CATEGORY OF CITED DOCUMENTS</b><br>X : particularly relevant if taken alone<br>Y : particularly relevant if combined with another document of the same category<br>A : technological background<br>O : non-written disclosure<br>P : intermediate document<br>T : theory or principle underlying the invention<br>E : earlier patent document, but published on, or after the filing date<br>D : document cited in the application<br>L : document cited for other reasons<br>Δ : member of the same patent family, corresponding document |   |  |   |

EPO FORM 1501 (04/92) (page 1)